



TRANSLATION

I, Naoko Namba, residing at 2-5-15-514, Honcho, Kawaguchi-shi,
Saitama, Japan, state:

that I know well both the Japanese and English languages; that I translated, from Japanese into English, Japanese Patent Application No. 2000-299231, filed on September 29, 2000; and that the attached English translation is a true and accurate translation to the best of my knowledge and belief.

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[What is claimed is]

5 [Claim 1] A lightsensitive material package comprising a silver halide color photographic lightsensitive material having at least one each of a red-sensitive, green-sensitive and blue-sensitive silver halide emulsion layer on a support and having 10 ISO speed of 640 or more, the silver halide color photographic lightsensitive material being arranged in a common gas-phase atmosphere and sealed in the lightsensitive material package together with a plastic material member, characterized in that the plastic 15 material member is that produced from a resin to which a substance capable of adsorbing a substance having an adverse effect on a photographic property has been supplementally added prior to molding thereof.

[Claim 2] A lightsensitive material package

comprising a silver halide color photographic

lightsensitive material having at least one each of a

red-sensitive, green-sensitive and blue-sensitive

silver halide emulsion layer on a support and having a

silver content of 6 to 10 g/m², the silver halide color

photographic lightsensitive material being arranged in

a common gas-phase atmosphere and sealed in the

lightsensitive material package together with a plastic

material member, characterized in that the plastic material member is that produced from a resin to which a substance capable of adsorbing a substance having an adverse effect on a photographic property has been supplementally added prior to molding thereof.

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[Claim 3] A lightsensitive material package comprising a silver halide color photographic lightsensitive material having at least one each of a red-sensitive, green-sensitive and blue-sensitive silver halide emulsion layer on a support and having the total thickness of all hydrophilic colloid layers of the silver halide color photographic lightsensitive material on its side of the lightsensitive silver halide layers of 22 μm or more, the silver halide color photographic lightsensitive material being arranged in a common gas-phase atmosphere and sealed in the lightsensitive material package together with a plastic material member, characterized in that the plastic material member is that produced from a resin to which a substance capable of adsorbing a substance having an adverse effect on a photographic property has been supplementally added prior to molding thereof.

[Claim 4] The lightsensitive material package according to claim 1, characterized in that a silver content of the silver halide color photographic light sensitive material is 6 to 10 g/m^2 .

[Claim 5] The lightsensitive material package

according to claim 4, characterized in that the total thickness of all hydrophilic colloid layers of the silver halide color photographic lightsensitive material on its side of the lightsensitive silver halide layers is 22 μm or more.

[Claim 6] A lightsensitive material package comprising a silver halide color photographic lightsensitive material having at least one each of a red-sensitive, green-sensitive and blue-sensitive silver halide emulsion layer on a support and having ISO speed of 640 or more, the silver halide color photographic lightsensitive material being arranged in a common gas-phase atmosphere and sealed in the lightsensitive material package together with a plastic material member, characterized in that the plastic material member is that produced from a resin to which a compound represented by the following general formula (TS-I) or (TS-II) has been supplementally added prior to molding thereof:

20 [Chem 1]

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$$R^{6}$$
 R^{2}
 R^{13}
 R^{10}
 R^{10}

in the formula (TS-I), R^1 represents a hydrogen atom, a substituted or unsubstituted alkyl group (including cycloalkyl and bicycloalkyl groups),

substituted or unsubstituted alkenyl group (including cycloalkenyl and bicycloalkenyl groups), substituted or unsubstituted aryl group, substituted or unsubstituted heterocyclic group, substituted or unsubstituted acyl group, substituted or unsubstituted alkoxycarbonyl 5 group (including those whose alkyl moiety is cycloalkyl or bicycloalkyl), substituted or unsubstituted aryloxycarbonyl group, substituted or unsubstituted alkylsulfonyl group (including cycloalkylsulfonyl and 10 bicycloalkylsulfonyl groups), substituted or unsubstituted arylsulfonyl group, substituted or unsubstituted phosphino group, substituted or unsubstituted phosphinoyl group, or a group of the formula $-\text{Si}(\mathbb{R}^{21})(\mathbb{R}^{22})(\mathbb{R}^{23})$, wherein each of \mathbb{R}^{21} , \mathbb{R}^{22} and \mathbb{R}^{23} independently represents a substituted or 15 unsubstituted alkyl group, substituted or unsubstituted aryl group, substituted or unsubstituted alkoxy group, substituted or unsubstituted alkenyloxy group, or substituted or unsubstituted aryloxy group; $-x^{1}$ represents -O-, -S- or -N(\mathbb{R}^{24})-, wherein \mathbb{R}^{24} has the 20 same meaning as R^1 ; and R^2 , R^3 , R^4 , R^5 and R^6 may be the same or different from each other, and each thereof represents a hydrogen atom or a substituent, provided that R^1 and R^2 , or R^{24} and R^6 , or R^1 and R^{24} , may be 25 bonded with each other to thereby form a 5- to 7membered ring, provided that R^2 and R^3 , or R^3 and R^4 , or \mathbb{R}^4 and \mathbb{R}^5 , or \mathbb{R}^5 and \mathbb{R}^6 , may be bonded with each

other to thereby form a 5- to 7-membered ring, or spiro ring or bicyclo ring, and provided that R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^{24} are not simultaneously hydrogen atoms; and

5 in the formula (TS-II), each of R^{11} , R^{12} , R^{13} and ${\it R}^{14}$ independently represents a hydrogen atom, an alkyl group (including cycloalkyl and bicycloalkyl groups), or alkenyl group (including cycloalkenyl and bicycloalkenyl groups), provided that R^{11} and R^{12} , or ${\bf R}^{13}$ and ${\bf R}^{14}$, may be bonded with each other to thereby 10 form a 5- to 7-membered ring; X^2 represents a hydrogen atom, an alkyl group (including cycloalkyl and bicycloalkyl groups), alkenyl group (including cycloalkenyl and bicycloalkenyl groups), alkoxy group (including cycloalkyloxy and bicycloalkyloxy groups), 15 alkenyloxy group (including cycloalkyenyloxy and bicycloalkenyloxy groups), alkyl- and alkenyloxycarbonyl groups (including those whose alkyl moiety is cycloalkyl and bicycloalkyl, and those whose alkenyl moiety is cycloalkenyl and bicycloalkenyl), 20 aryloxycarbonyl group, acyl group, acyloxy group, alkyloxycarbonyloxy group (including those whose alkyl moiety is cycloalkyl and bicycloalkyl), alkenyloxycarbonyloxy group (including those whose 25 alkenyl moiety is cycloalkyenl and bicycloalkyenyl), aryloxycarbonyloxy group, alkyl- and alkenylsulfonyl groups (including those whose alkyl moiety is

cycloalkyl and bicycloalkyl, and those whose alkenyl moiety is cycloalkenyl and bicycloalkenyl), arylsulfonyl group, alkyl— and alkenylsulfinyl groups (including those whose alkyl moiety is cycloalkyl and bicycloalkyl, and those whose alkenyl moiety is cycloalkenyl and bicycloalkenyl), arylsulfinyl group, sulfamoyl group, carbamoyl group, hydroxyl group, or oxy radical group; and X³ represents a group of nonmetallic atoms required for forming a 5- to 7-membered ring.

[Claim 7] A lightsensitive material package comprising a silver halide color photographic lightsensitive material having at least one each of a red-sensitive, green-sensitive and blue-sensitive silver halide emulsion layer on a support and having a silver content of 6 to 10 g/m², the silver halide color photographic lightsensitive material being arranged in a common gas-phase atmosphere and sealed in the lightsensitive material package together with a plastic material member, characterized in that the plastic material member is that produced from a resin to which the compound represented by the general formula (TS-I) or (TS-II) described in claim 6 has been supplementally added prior to molding thereof.

[Claim 8] A lightsensitive material package comprising a silver halide color photographic lightsensitive material having at least one each of a

red-sensitive, green-sensitive and blue-sensitive silver halide emulsion layer on a support and having the total thickness of all hydrophilic colloid layers of the silver halide color photographic lightsensitive material on its side of the lightsensitive silver halide layers of 22 µm or more, the silver halide color photographic lightsensitive material being arranged in a common gas-phase atmosphere and sealed in the lightsensitive material package together with a plastic material member, characterized in that the plastic material member is that produced from a resin to which the compound represented by the general formula (TS-I) or (TS-II) described in claim 6 has been supplementally added prior to molding thereof.

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[Claim 9] The lightsensitive material package according to claim 6, characterized in that a silver content of the silver halide color photographic light sensitive material is 6 to 10 g/m^2 .

[Claim 10] The lightsensitive material package according to claim 9, characterized in that the total thickness of all hydrophilic colloid layers of the silver halide color photographic lightsensitive material on its side of the lightsensitive silver halide layers is 22 μ m or more.

[Claim 11] The lightsensitive material package according to any one of claims 1 to 5, characterized in that the plastic material is that produced from a resin

to which a compound represented by the following general formula (TS-I) or (TS-II) has been supplementally added prior to molding thereof.

[Claim 12] The lightsensitive material package according to any one of claims 1 to 5 and 11, characterized in that the substance capable of adsorbing a substance having adverse effects on photographic properties is carbon black having an acetaldehyde gas equilibrium adsorption amount of 2 mg/g or more.

[Claim 13] The lightsensitive material package according to any one of claims 6 to 11, characterized in that a molecular weight of the compound represented by the general formula (TS-I) or (TS-II) is 230 or more. [Detailed Description of the Invention]

[0001]

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[Technical Field of the Invention]

The present invention relates to a lightsensitive material package. More particularly, the present invention relates to a lightsensitive material package in which a color photographic lightsensitive material having an emulsion of high aspect ratio is arranged in a common gas phase atmosphere and sealed with recycled plastic material members constituted of reclaimed resins, the above reclaimed resins obtained through remelting of, for example, plastic material members made of thermoplastic resins. The present invention

relates especially to a lightsensitive material package in which reclaimed resin of polystyrene is used.

[0002]

[Prior Art]

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Reclaimed resins, as plastic material members or a container, are used in, for example, a body of lens-fitted packaging unit and a spool or core of 35 mm patrone. Reclaimed resins are further used in, other than those accommodated together with a lightsensitive material, a photographic film case and other accommodating items.

[0003]

Further description will be made with reference to a lightsensitive material packaging unit including a 15 built-in color negative photographic lightsensitive material and furnished with an exposure function (known as a lens-fitted film), now widespread for its convenience. Generally, the cartridge of lens-fitted lightsensitive material packaging unit is produced by 20 molding a high impact polystyrene resin comprising a polystyrene resin (hereinafter referred to as "PS resin") to which a butadiene rubber polymerization has been carried out to thereby impart impact resistance, which high impact PS resin contains carbon black for 25 light shielding and various additives for moldability enhancement.

[0004]

This cartridge of lens-fitted lightsensitive material packaging unit, because of its built-in photosensitive material, is constituted of resins selected with the care that there should be no fogging or abnormal sensitivity attributed to gases released from impurities or resin ingredients contained therein.

[0005]

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Each lens-fitted lightsensitive material packaging unit, after photographing, is sent to a laboratory, where the photosensitive material having undergone photographing is taken out, developed and fixed on a photographic paper.

The packaging unit from which the photosensitive material has been removed, for the purpose of environmental protection and resource saving, is collected, converted to reclaimed resins through steps such as disassembly, classification, crushing and melting, and reutilized as a molding material for the cartridge of lens-fitted lightsensitive material packaging unit or the like.

[0006]

With respect to reclaimed resins, the use thereof in parts brought into contact with the photographic lightsensitive material has been restricted because of the reclamation from products collected on the market, in particular because of the concern about any increase of the occurrence of photographically harmful

substances attributed to resin pyrolysis by an increase of heat history and also the concern about the inclusion of substances harmful to photographic lightsensitive material as described in Jpn. Pat. Appln. KOKAI Publication No. (hereinafter referred to as JP-A-) 5-165154.

Further, a high speed photographic material and photographic material using a lot of silver halide, and photographic material having a large photographic thickness are easier to be influenced by such a harmful substance to cause the deterioration in photographic properties. Thus, use of the reclaimed resin has been restricted similarly.

[0007]

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15 With respect to harmful substances from thermoplastic resins which have adverse effects on photographic lightsensitive materials, it is presumed that, as described in JP-A's-6-130565 and 6-67356, aldehydes, ketones, free sulfur, cyanide and other compounds resulting from resin pyrolysis are gasified and adsorbed on film surface to thereby denature the silver halides of the film with the result that the photographic properties are changed.

The generation of harmful substances from such resins would be attributable to carbon black, various additives and rubber components and, with respect to reclaimed resins, to impurities adhered thereto on the

market.

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[8000]

With respect to gases which are harmful to photographic lightsensitive materials, it is described in JP-A-6-130565 that, the greater the heat history frequency at molding or extrusion in the presence of an antioxidant, the greater the evaporation of impurities, so that the amount of antioxidant is less in the reclaimed resin than in the virgin resin.

However, when a fog test is conducted for a high speed photographic material or photographic material using a large amount of silver in molded products of reclaimed resin and virgin resin, it was revealed that when the virgin resin is used no adverse effect arose, while when the reclaimed resin is used the adverse effect arose so largely that the photographic materials were unable to practically used.

[0009]

reclaimed resin, the heat history is increased to thereby reduce the amount of antioxidant and cause new photographically harmful gases to occur from the PS resin containing rubber components. Further, it is described in JP-A-6-67356 that harmful substances are suppressed by the addition of an antioxidant or the like. However, in the use of reclaimed resin, the above component reduction occurs with the result that

the effect exerted by the virgin resin is diminished. [0010]

The present invention is aimed to eradicate the adverse effects of the molded material or container to the photographic lightsensitive material by supplementally adding a substance capable of adsorbing a photographically harmful substance and a compound capable of suppressing the generation of a photographically harmful substance in reclaimed resin during the preparation of the reclaimed resin or immediately before molding of the reclaimed resin.

[0011]

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[Objects of the Invention]

It is an object of the present invention to 15 provide a lightsensitive material package wherein a molding containing a substance capable of adsorbing harmful substances, in particular gasified harmful substances, in reclaimed resins or capable of suppressing the occurrence thereof, which molding has thus no adverse effects on photographic lightsensitive 20 materials, in particular a photographic lightsensitive material of high-speed lightsensitive material and a light sensitive material having a large use amount of silver and a lightsensitive material having a large 25 film thickness of the photographic material, is accommodated in order to expand the use of reclaimed resins in plastic material members.

[0012]

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[Means for Achieving the Objects]

The above objects were attained by preparing reclaimed resin by supplementally adding an absorbent to a photographically harmful substance and a compound of suppressing the generation of the harmful substance from the reclaimed resin during the production thereof or immediately before the processing of molding, and mixing them.

As a result of extensive study, the present inventors have found the means to solve the problems by the following methods.

[0013]

A lightsensitive material package comprising a silver halide color photographic lightsensitive 15 material having at least one each of a red-sensitive, green-sensitive and blue-sensitive silver halide emulsion layer on a support and having ISO speed of 640 or more, the silver halide color photographic 20 lightsensitive material being arranged in a common gasphase atmosphere and sealed in the lightsensitive material package together with a plastic material member, characterized in that the plastic material member is that produced from a resin to which a 25 substance capable of adsorbing a substance having an adverse effect on a photographic property has been supplementally added prior to molding thereof.

[0014]

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a silver halide color photographic lightsensitive material having at least one each of a red-sensitive, green-sensitive and blue-sensitive silver halide emulsion layer on a support and having a silver content of 6 to 10 g/m², the silver halide color photographic lightsensitive material being arranged in a common gasphase atmosphere and sealed in the lightsensitive material member, characterized in that the plastic material member is that produced from a resin to which a substance capable of adsorbing a substance having an adverse effect on a photographic property has been supplementally added prior to molding thereof.

[0015]

(3) A lightsensitive material package comprising a silver halide color photographic lightsensitive material having at least one each of a red-sensitive, green-sensitive and blue-sensitive silver halide emulsion layer on a support and having the total thickness of all hydrophilic colloid layers of the silver halide color photographic lightsensitive material on its side of the lightsensitive silver halide layers of 22 μm or more, the silver halide color photographic lightsensitive material being arranged in a common gas-phase atmosphere and sealed in the

lightsensitive material package together with a plastic material member, characterized in that the plastic material member is that produced from a resin to which a substance capable of adsorbing a substance having an adverse effect on a photographic property has been supplementally added prior to molding thereof.

[0016]

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(4) The lightsensitive material package according to (1) above, characterized in that a silver content of the silver halide color photographic light sensitive material is 6 to 10 q/m^2 .

[0017]

(5) The lightsensitive material package according to (4) above, characterized in that the total thickness of all hydrophilic colloid layers of the silver halide color photographic lightsensitive material on its side of the lightsensitive silver halide layers is 22 μm or more.

[0018]

20 (6) A lightsensitive material package comprising a silver halide color photographic lightsensitive material having at least one each of a red-sensitive, green-sensitive and blue-sensitive silver halide emulsion layer on a support and having ISO speed of 640 or more, the silver halide color photographic lightsensitive material being arranged in a common gasphase atmosphere and sealed in the lightsensitive

material package together with a plastic material member, characterized in that the plastic material member is that produced from a resin to which a compound represented by the following general formula (TS-I) or (TS-II) has been supplementally added prior to molding thereof:

[0019]

[Chem 2]

$$R^{6}$$
 R^{2}
 R^{13}
 R^{10}
 R^{11}
 R^{12}
 R^{12}
 R^{12}
 R^{13}
 R^{14}
 R^{12}
 R^{12}
 R^{12}
 R^{13}
 R^{14}
 R^{14}
 R^{15}
 R^{15}
 R^{15}
 R^{15}

10 [0020]

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In the formula (TS-I), R1 represents a hydrogen atom, a substituted or unsubstituted alkyl group (including cycloalkyl and bicycloalkyl groups), substituted or unsubstituted alkenyl group (including cycloalkenyl and bicycloalkenyl groups), substituted or unsubstituted or unsubstituted or unsubstituted heterocyclic group, substituted or unsubstituted acyl group, substituted or unsubstituted acyl group, substituted or unsubstituted alkoxycarbonyl group (including those whose alkyl moiety is cycloalkyl or bicycloalkyl), substituted or unsubstituted aryloxycarbonyl group, substituted or unsubstituted alkylsulfonyl group, substituted or unsubstituted alkylsulfonyl group (including cycloalkylsulfonyl and bicycloalkylsulfonyl groups), substituted or unsubstituted or unsubstituted arylsulfonyl group, substituted or

unsubstituted phosphino group, substituted or unsubstituted phosphinoyl group, or a group of the formula $-Si(R^{21})(R^{22})(R^{23})$, wherein each of R^{21} , R^{22} and R^{23} independently represents a substituted or unsubstituted alkyl group, substituted or unsubstituted aryl group, substituted or unsubstituted alkoxy group, substituted or unsubstituted alkenyloxy group, or substituted or unsubstituted aryloxy group; $-x^{1}$ represents -O-, -S- or -N(\mathbb{R}^{24})-, wherein \mathbb{R}^{24} has the same meaning as R^1 ; and R^2 , R^3 , R^4 , R^5 and R^6 may be the same or different from each other, and each thereof represents a hydrogen atom or a substituent, provided that R^1 and R^2 , or R^{24} and R^6 , or R^1 and R^{24} , may be bonded with each other to thereby form a 5- to 7membered ring, provided that R^2 and R^3 , or R^3 and R^4 , or \mathbb{R}^4 and \mathbb{R}^5 , or \mathbb{R}^5 and \mathbb{R}^6 , may be bonded with each other to thereby form a 5- to 7-membered ring, or spiro ring or bicyclo ring, and provided that R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^{24} are not simultaneously hydrogen atoms. [0021]

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In the formula (TS-II), each of R¹¹, R¹², R¹³ and R¹⁴ independently represents a hydrogen atom, an alkyl group (including cycloalkyl and bicycloalkyl groups), or alkenyl group (including cycloalkenyl and bicycloalkenyl groups), provided that R¹¹ and R¹², or R¹³ and R¹⁴, may be bonded with each other to thereby form a 5- to 7-membered ring; x^2 represents a hydrogen

atom, an alkyl group (including cycloalkyl and bicycloalkyl groups), alkenyl group (including cycloalkenyl and bicycloalkenyl groups), alkoxy group (including cycloalkyloxy and bicycloalkyloxy groups), alkenyloxy group (including cycloalkyenyloxy and 5 bicycloalkenyloxy groups), alkyl- and alkenyloxycarbonyl groups (including those whose alkyl moiety is cycloalkyl and bicycloalkyl, and those whose alkenyl moiety is cycloalkenyl and bicycloalkenyl), aryloxycarbonyl group, acyl group, acyloxy group, alkyloxycarbonyloxy group (including those whose alkyl moiety is cycloalkyl and bicycloalkyl), alkenyloxycarbonyloxy group (including those whose alkenyl moiety is cycloalkyenl and bicycloalkyenyl), aryloxycarbonyloxy group, alkyl- and alkenylsulfonyl groups (including those whose alkyl moiety is cycloalkyl and bicycloalkyl, and those whose alkenyl moiety is cycloalkenyl and bicycloalkenyl), arylsulfonyl group, alkyl- and alkenylsulfinyl groups (including those whose alkyl moiety is cycloalkyl and bicycloalkyl, and those whose alkenyl moiety is cycloalkenyl and bicycloalkenyl), arylsulfinyl group, sulfamoyl group, carbamoyl group, hydroxyl group, or oxy radical group; and X^3 represents a group of nonmetallic atoms required for forming a 5- to 7membered ring.

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a silver halide color photographic lightsensitive material having at least one each of a red-sensitive, green-sensitive and blue-sensitive silver halide emulsion layer on a support and having a silver content of 6 to 10 g/m², the silver halide color photographic lightsensitive material being arranged in a common gasphase atmosphere and sealed in the lightsensitive material member, characterized in that the plastic material member is that produced from a resin to which the compound represented by the general formula (TS-I) or (TS-II) described in (6) above has been supplementally added prior to molding thereof.

15 [0023]

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a silver halide color photographic lightsensitive material having at least one each of a red-sensitive, green-sensitive and blue-sensitive silver halide emulsion layer on a support and having the total thickness of all hydrophilic colloid layers of the silver halide color photographic lightsensitive material on its side of the lightsensitive silver halide layers of 22 μm or more, the silver halide color photographic lightsensitive material being arranged in a common gas-phase atmosphere and sealed in the lightsensitive material package together with a plastic

material member, characterized in that the plastic material member is that produced from a resin to which the compound represented by the general formula (TS-I) or (TS-II) described in (6) above has been supplementally added prior to molding thereof.

[0024]

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(9) The lightsensitive material package according to (6) above, characterized in that a silver content of the silver halide color photographic light sensitive material is 6 to 10 g/m^2 .

[0025]

(10) The lightsensitive material package according to (9) above, characterized in that the total thickness of all hydrophilic colloid layers of the silver halide color photographic lightsensitive material on its side of the lightsensitive silver halide layers is 22 μ m or more.

[0026]

- (11) The lightsensitive material package

 20 according to any one of (1) to (5) above, characterized in that the plastic material is that produced from a resin to which a compound represented by the following general formula (TS-I) or (TS-II) has been supplementally added prior to molding thereof.
- 25 [0027]
 - (12) The lightsensitive material package according to any one of (1) to (5) and (11) above,

characterized in that the substance capable of adsorbing a substance having adverse effects on photographic properties is carbon black having an acetaldehyde gas equilibrium adsorption amount of 2 mg/g or more.

[0028]

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(13) The lightsensitive material package according to any one of (6) to (11) above, characterized in that a molecular weight of the compound represented by the general formula (TS-I) or (TS-II) is 230 or more.

[0029]

[Embodiments of the Invention]

The present invention will be explained in more detail below.

The compound represented by the following general formula (TS-I) or (TS-II) will be explained in detail.

In the formula (TS-I), R¹ represents a hydrogen

atom, a substituted or unsubstituted alkyl group

(including cycloalkyl and bicycloalkyl groups),

substituted or unsubstituted alkenyl group (including

cycloalkenyl and bicycloalkenyl groups), substituted or

unsubstituted aryl group, substituted or unsubstituted

25 heterocyclic group, substituted or unsubstituted acyl

group, substituted or unsubstituted alkoxycarbonyl

group (including those whose alkyl moiety is cycloalkyl

or bicycloalkyl), substituted or unsubstituted aryloxycarbonyl group, substituted or unsubstituted alkylsulfonyl group (including cycloalkylsulfonyl and bicycloalkylsulfonyl groups), substituted or 5 unsubstituted arylsulfonyl group, substituted or unsubstituted phosphino group, substituted or unsubstituted phosphinoyl group, or a group of the formula $-\text{Si}(\mathbb{R}^{21})(\mathbb{R}^{22})(\mathbb{R}^{23})$, wherein each of \mathbb{R}^{21} , \mathbb{R}^{22} and \mathbb{R}^{23} independently represents a substituted or unsubstituted alkyl group, substituted or unsubstituted 10 aryl group, substituted or unsubstituted alkoxy group, substituted or unsubstituted alkenyloxy group, or substituted or unsubstituted aryloxy group; $-x^{1}$ represents -O-, -S- or -N(\mathbb{R}^{24})-, wherein \mathbb{R}^{24} has the same meaning as R^1 ; and R^2 , R^3 , R^4 , R^5 and R^6 may be 15 the same or different from each other, and each thereof represents a hydrogen atom or a substituent, provided that ${\rm R}^1$ and ${\rm R}^2$, or ${\rm R}^{24}$ and ${\rm R}^6$, or ${\rm R}^1$ and ${\rm R}^{24}$, may be bonded with each other to thereby form a 5- to 7membered ring, provided that R^2 and R^3 , or R^3 and R^4 , or \mathbb{R}^4 and \mathbb{R}^5 , or \mathbb{R}^5 and \mathbb{R}^6 , may be bonded with each other to thereby form a 5- to 7-membered ring, or spiro ring or bicyclo ring, and provided that R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^{24} are not simultaneously hydrogen atoms. [0031]

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In the formula (TS-II), each of R^{11} , R^{12} , R^{13} and ${f R}^{14}$ independently represents a hydrogen atom, an alkyl

group (including cycloalkyl and bicycloalkyl groups), or alkenyl group (including cycloalkenyl and bicycloalkenyl groups), provided that R^{11} and R^{12} , or ${\bf R}^{13}$ and ${\bf R}^{14}$, may be bonded with each other to thereby form a 5- to 7-membered ring; X^2 represents a hydrogen 5 atom, an alkyl group (including cycloalkyl and bicycloalkyl groups), alkenyl group (including cycloalkenyl and bicycloalkenyl groups), alkoxy group (including cycloalkyloxy and bicycloalkyloxy groups), 10 alkenyloxy group (including cycloalkyenyloxy and bicycloalkenyloxy groups), alkyl- and alkenyloxycarbonyl groups (including those whose alkyl moiety is cycloalkyl and bicycloalkyl, and those whose alkenyl moiety is cycloalkenyl and bicycloalkenyl), aryloxycarbonyl group, acyl group, acyloxy group, 15 alkyloxycarbonyloxy group (including those whose alkyl moiety is cycloalkyl and bicycloalkyl), alkenyloxycarbonyloxy group (including those whose alkenyl moiety is cycloalkyenl and bicycloalkyenyl), aryloxycarbonyloxy group, alkyl- and alkenylsulfonyl 20 groups (including those whose alkyl moiety is cycloalkyl and bicycloalkyl, and those whose alkenyl moiety is cycloalkenyl and bicycloalkenyl), arylsulfonyl group, alkyl- and alkenylsulfinyl groups 25 (including those whose alkyl moiety is cycloalkyl and bicycloalkyl, and those whose alkenyl moiety is cycloalkenyl and bicycloalkenyl), arylsulfinyl group,

sulfamoyl group, carbamoyl group, hydroxyl group, or oxy radical group; and \mathbf{X}^3 represents a group of nonmetallic atoms required for forming a 5- to 7-membered ring.

5 [0032]

The present invention will be described in detail. In the formula (TS-I), \mathbb{R}^1 represents a hydrogen atom; a substituted or unsubstituted alkyl group (including cycloalkyl and bicycloalkyl groups), (preferably those having 1 to 30 carbon atoms, e.g., 10 methyl, ethyl, n-butyl, cyclohexyl, and bicyclo[1,2,2]heptan-2-yl); substituted or unsubstituted alkenyl group (including cycloalkenyl and bicycloalkenyl groups) (preferably those having 3 to 30 carbon atoms, e.g., allyl, geranyl, and 2-cyclohexen-1-15 yl); substituted or unsubstituted aryl group (preferably those having 6 to 30 carbon atoms, e.g., phenyl, p-tolyl); substituted or unsubstituted heterocyclic group (preferably 5- or 6-membered, substituted or unsubstituted, aromatic or nonaromatic 20 heterocycle from which a hydrogen atom is removed, more preferably, 5- or 6-membered aromatic heterocycle having 3 to 30 carbon atoms from which a hydrogen atom is removed, e.g., 2-furyl, 2-thienyl, and 2pyrimidinyl); substituted or unsubstituted acyl group 25 (preferably those having 1 to 30 carbon atoms, e.g., formyl, acetyl, and pivaloyl); substituted or

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unsubstituted alkoxycarbonyl group (preferably those having 2 to 30 carbon atoms, e.g., methoxycarbonyl, ethoxycarbonyl, and decyloxycarbonyl); substituted or unsubstituted aryloxycarbonyl group (preferably those having 7 to 30 carbon atoms, e.g., phenoxycarbonyl); substituted or unsubstituted alkylsulfonyl group (including cycloalkylsulfonyl and bicycloalkylsulfonyl) (preferably those having 1 to 30 carbon atoms, e.g., methanesulfonyl, ethanesulfonyl, and cyclohexylsulfonyl); substituted or unsubstituted arylsulfonyl group (preferably those having 6 to 30 carbon atoms e.g., toluenesulfonyl, and benzenesulfonyl), substituted or unsubstituted phosphino group (preferably those having 0 to 30 carbon. atoms, e.g., diphenylphosphino); substituted or unsubstituted phosphinoyl group (preferably those having 0 to 30 carbon atoms, e.g., diphenylphosphinoyl); or $-SiR^{21}R^{22}R^{23}$, wherein each of $\ensuremath{\text{R}^{21}}\xspace$, $\ensuremath{\text{R}^{22}}\xspace$ and $\ensuremath{\text{R}^{23}}\xspace$ independently represents a substituted or unsubstituted alkyl group (preferably those having 1 to 30 carbon atoms, e.g., methyl), substituted or unsubstituted aryl group (preferably those having 6 to 30 carbon atoms, e.g., phenyl), substituted or unsubstituted alkoxy group (preferably those having 1 to 30 carbon atoms, e.g., methoxy), substituted or unsubstituted alkenyloxy group (preferably those having 3 to 30 carbon atoms, e.g., geranyloxy), or substituted

or unsubstituted aryloxy group (preferably those having 6 to 30 carbon atoms, e.g., phenoxy).

[0033]

 ${\bf R}^2$, ${\bf R}^3$, ${\bf R}^4$, ${\bf R}^5$ and ${\bf R}^6$ independently represent a 5 hydrogen, or halogen atom; or an alkyl group (including cycloalkyl and bicycloalkyl groups); alkenyl group (including cycloalkenyl and bicycloalkenyl groups); alkynyl group; aryl group; heterocyclic group; cyano group; hydroxyl group; nitro group; carboxyl group; 10 alkoxy group; aryloxy group; silyloxy group; heterocyclic oxy group; acyloxy group; carbamoyloxy group; alkoxycarbonyloxy group; aryloxycarbonyloxy group; amino group (including an anilino group); acylamino group; aminocarbonylamino group; 15 alkoxycarbonylamino group; aryloxycarbonylamino group; sulfamoylamino group; alkyl- and arylsulfonylamino groups; mercapto group; alkylthio group; arylthio group; heterocyclic thio group; sulfamoyl group; sulfo group; alkyl- and arylsulfinyl groups; alkyl- and arylsulfonyl groups; acyl group; aryloxycarbonyl group; 20 alkoxycarbonyl group; carbamoyl group; aryl- and heterocyclic azo groups; imido group; phosphino group; phosphinyl group; phosphinyloxy group; phosphinylamino group; or silyl group.

25 [0034]

More specifically, R^2 , R^3 , R^4 , R^5 and R^6 independently represent a hydrogen atom; or a halogen

atom (e.g., a chlorine atom, bromine atom, and iodine atom); or an alkyl group {which represents a straight-chain, branched, or cyclic, substituted or unsubstituted alkyl group. Examples are an alkyl group 5 (preferably those having 1 to 30 carbon atoms, e.g., methyl, ethyl, n-propyl, isopropyl, t-butyl, n-octyl, eicosyl, 2-chloroethyl, 2-cyanoethyl, and 2-ethylhexyl), a cycloalkyl group (preferably substituted or unsubstituted cycloalkyl group having 3 to 30 carbon 10 atoms, e.g., cyclohexyl, cyclopentyl, and 4-n-dodecylcyclohexyl), a bicycloalkyl group (preferably a substituted or unsubstituted bicycloalkyl group having 5 to 30 carbon atoms, i.e., a monovalent group obtained by removing one hydrogen atom from a 15 bicycloalkane having 5 to 30 carbon atoms. Examples are bicyclo[1,2,2]heptane-2-yl and bicyclo[2,2,2]octane-3-yl). Also an alkyl group having more cyclic structure such as a tricyclic alkyl group is included. The alkyl group to be described below, 20 such as the alkyl group of an alkylthio group, also includes the concept of the alkyl group mentioned above.); alkenyl group {which represents a straight-chain, branched, or cyclic, substituted or unsubstituted alkenyl group. Examples are an alkenyl 25 group (preferably a substituted or unsubstituted alkenyl group having 2 to 30 carbon atoms, e.g., vinyl, allyl, prenyl, geranyl, and oleyl), cycloalkenyl group

(preferably a substituted or unsubstituted cycloalkenyl group having 3 to 30 carbon atoms, i.e., a monovalent group obtained by removing one hydrogen atom from a cycloalkene having 3 to 30 carbon atoms. Examples are 5 2-cyclopentene-1-yl and 2-cyclohexene-1-yl), bicycloalkenyl group (a substituted or unsubstituted bicycloalkenyl group, preferably a substituted or unsubstituted bicycloalkenyl group having 5 to 30 carbon atoms, i.e., a monovalent group obtained by removing one hydrogen atom from bicycloalkene having 10 one double bond. Examples are bicyclo[2,2,1]hept-2-ene-1-yl and bicyclo[2,2,2]oct-2-ene-4-yl)}; an alkynyl group (preferably a substituted or unsubstituted alkynyl group having 2 to 30 carbon atoms, e.g., ethynyl, 15 propargyl, and trimethylsilylethynyl); aryl group (preferably a substituted or unsubstituted aryl group having 6 to 30 carbon atoms, e.g., phenyl, p-tolyl, naphthyl, m-chlorophenyl, and o-hexadecanoylaminophenyl); heterocyclic group 20 (preferably a monovalent group obtained by removing one hydrogen atom from a 5- or 6-membered, substituted or unsubstituted, aromatic or nonaromatic heterocyclic compound, and more preferably, a 5- or 6-membered aromatic heterocyclic group having 3 to 30 carbon atoms. 25 Examples are 2-furyl, 2-thienyl, 2-pyrimidinyl, and 2-benzothiazolyl); cyano group; hydroxyl group; nitro

group; carboxyl group; and alkoxy group (preferably a substituted or unsubstituted alkoxy group having 1 to 30 carbon atoms, e.g., methoxy, ethoxy, isopropoxy, t-butoxy, n-octyloxy, and 2-methoxyethoxy); an aryloxy 5 group (preferably a substituted or unsubstituted aryloxy group having 6 to 30 carbon atoms, e.g., phenoxy, 2-methylphenoxy, 4-t-butylphenoxy, 3-nitrophenoxy, and 2-tetradecanoylaminophenoxy), silyloxy group (preferably a silyloxy group having 3 to 10 20 carbon atoms, e.g., trimethylsilyloxy and t-butyldimethylsilyloxy); heterocyclic oxy group (preferably a substituted or unsubstituted heterocyclic oxy group having 2 to 30 carbon atoms, e.g., 1-phenyltetrazole-5-oxy and 2-tetrahydropyranyloxy); 15 and acyloxy group (preferably a formyloxy group, a substituted or unsubstituted alkylcarbonyloxy group having 2 to 30 carbon atoms, and a substituted or unsubstituted arylcarbonyloxy group having 7 to 30 carbon atoms, e.g., formyloxy, acetyloxy, pivaloyloxy, 20 stearoyloxy, benzoyloxy, and p-methoxyphenylcarbonyloxy); a carbamoyloxy group (preferably a substituted or unsubstituted carbamoyloxy group having 1 to 30 carbon atoms, e.g., N, N-dimethylcarbamoyloxy, N, N-diethylcarbamoyloxy, 25 . morpholinocarbonyloxy, N,N-di-n-octylaminocarbonyloxy, and N-n-octylcarbamoyloxy); alkoxycarbonyloxy group (preferably a substituted or unsubstituted

alkoxycarbonyloxy group having 2 to 30 carbon atoms, e.g., methoxycarbonyloxy, ethoxycarbonyloxy, t-butoxycarbonyloxy, and n-octylcarbonyloxy); and aryloxycarbonyloxy group (preferably a substituted or unsubstituted aryloxycarbonyloxy group having 7 to 305 carbon atoms, e.g., phenoxycarbonyloxy, p-methoxyphenoxycarbonyloxy, and p-(n-hexadecyloxy)phenoxycarbonyloxy); an amino group (preferably an unsubstituted amino group, a substituted or unsubstituted alkylamino group having 1 to 30 carbon 10 atoms, and a substituted or unsubstituted anilino group having 6 to 30 carbon atoms, e.g., amino, methylamino, dimethylamino, anilino, N-methyl-anilino, and diphenylamino); acylamino group (preferably a 15 formylamino group, a substituted or unsubstituted alkylcarbonylamino group having 2 to 30 carbon atoms, and a substituted or unsubstituted arylcarbonylamino group having 7 to 30 carbon atoms, e.g., formylamino, acetylamino, pivaloylamino, lauroylamino, benzoylamino, and 3,4,5-tri-(n-octyloxyphenyl)carbonylamino); and 20 aminocarbonylamino group (preferably a substituted or unsubstituted aminocarbonylamino having 1 to 30 carbon atoms, e.g., carbamoylamino, N, N-dimethylaminocarbonylamino,

N,N-diethylaminocarbonylamino, and morpholinocarbonylamino); an alkoxycarbonylamino group (preferably a substituted or unsubstituted

alkoxycarbonylamino group having 2 to 30 carbon atoms, e.g., methoxycarbonylamino, ethoxycarbonylamino, t-butoxycarbonylamino, n-octadecyloxycarbonylamino, and N-methyl-methoxycarbonylamino); aryloxycarbonylamino group (preferably a substituted or unsubstituted 5 aryloxycarbonylamino group having 7 to 30 carbon atoms, e.g., phenoxycarbonylamino, p-chlorophenoxycarbonylamino, and m-(n-octyloxy)phenoxycarbonylamino); sulfamoylamino group (preferably a substituted or unsubstituted 10 sulfamoylamino group having 0 to 30 carbon atoms, e.g., sulfamoylamino, N,N-dimethylaminosulfonylamino, and N-n-octylaminosulfonylamino); an alkylsulfonylamino and arylsulfonylamino groups (preferably a substituted or unsubstituted alkylsulfonylamino having 1 to 30 carbon 15 atoms, and a substituted or unsubstituted arylsulfonylamino having 6 to 30 carbon atoms, e.g., methylsulfonylamino, butylsulfonylamino, phenylsulfonylamino, 2,3,5-trichlorophenylsulfonylamino, 20 and p-methylphenylsulfonylamino); mercapto group; alkylthio group (preferably a substituted or unsubstituted alkylthio group having 1 to 30 carbon atoms, e.g., methylthio, ethylthio, and n-hexadecylthio); arylthio group (preferably a substituted or unsubstituted arylthio group having 6 to 25 30 carbon atoms, e.g., phenylthio, p-chlorophenylthio, and m-methoxyphenylthio); and heterocyclic thio group

(preferably a substituted or unsubstituted heterocyclic thio group having 2 to 30 carbon atoms, to which an aromatic ring such as a benzene ring may be condensed, e.g., 2-benzothiazolylthio and

- 1-phenyl-tetrazole-5-ylthio); a sulfamoyl group (preferably a substituted or unsubstituted sulfamoyl group having 0 to 30 carbon atoms, e.g., N-ethylsulfamoyl, N-(3-dodecyloxypropyl)sulfamoyl, N,N-dimethylsulfamoyl, N-acetylsulfamoyl,
- N-benzoylsulfamoyl, N-(N'-phenylcarbamoyl)sulfamoyl);
 sulfo group; alkylsulfinyl and arylsulfinyl groups
 (preferably a substituted or unsubstituted
 alkylsulfinyl group having 1 to 30 carbon atoms, and a
 substituted or unsubstituted arylsulfinyl group having
- 6 to 30 carbon atoms, e.g., methylsulfinyl, ethylsulfinyl, phenylsulfinyl, and p-methylphenylsulfinyl); an alkylsulfonyl and arylsulfonyl groups (preferably a substituted or unsubstituted alkylsulfonyl group having 1 to 30 carbon atoms, and a substituted or unsubstituted arylsulfonyl
- group having 6 to 30 carbon atoms, e.g., methylsulfonyl, ethylsulfonyl, phenylsulfonyl, and p-methylphenylsulfonyl); acyl group (preferably a
- alkylcarbonyl group having 2 to 30 carbon atoms, a substituted or unsubstituted arylcarbonyl group having 7 to 30 carbon atoms, and a substituted or

formyl group, substituted or unsubstituted

unsubstituted heterocycliccarbonyl group, whose carbon atom in the heterocyclic ring bonds to the carbonyl group thereof, e.g., acetyl, pivaloyl, 2-chloroacetyl, stearoyl, benzoyl, p-(n-octyloxy)phenylcarbonyl, 2-5 pyridylcarbonyl and 2-furylcarbonyl); aryloxycarbonyl group (preferably a substituted or unsubstituted aryloxycarbonyl group having 7 to 30 carbon atoms, e.g., phenoxycarbonyl, o-chlorophenoxycarbonyl, m-nitrophenoxycarbonyl, and p-(t-butyl)phenoxycarbonyl); and an alkoxycarbonyl 10 group (e.g., a substituted or unsubstituted alkoxycarbonyl group having 2 to 30 carbon atoms, e.g., methoxycarbonyl, ethoxycarbonyl, t-butoxycarbonyl, and n-octadecyloxycarbonyl); a carbamoyl group (preferably 15 a substituted or unsubstituted carbamoyl having 1 to 30 carbon atoms, e.g., carbamoyl, N-methylcarbamoyl, N, N-dimethylcarbamoyl, N, N-di-(n-octyl)carbamoyl, and N-(methylsulfonyl)carbamoyl); arylazo and heterocyclic azo groups (preferably a substituted or unsubstituted 20 arylazo group having 6 to 30 carbon atoms, and a substituted or unsubstituted heterocyclic azo group having 3 to 30 carbon atoms, e.g., phenylazo, p-chlorophenylazo, and 5-ethylthio-1,3,4-thiadiazole-2-ylazo); imido group 25 (preferably N-succinimido and N-phthalimido); phosphino group (preferably a substituted or unsubstituted

phosphino group having 2 to 30 carbon atoms, e.g.,

dimethylphosphino, diphenylphosphino, and methylphenoxyphosphino); and phosphinyl group (preferably a substituted or unsubstituted phosphinyl group having 0 to 30 carbon atoms, e.g., phosphinyl, dioctyloxyphosphinyl, and diethoxyphosphinyl); a phosphinyloxy group (preferably a substituted or unsubstituted phosphinyloxy group having 2 to 30 carbon atoms, e.g., diphenoxyphosphinyloxy and dioctyloxyphosphinyloxy); phosphinylamino group (preferably a substituted or unsubstituted phosphinylamino group having 2 to 30 carbon atoms, e.g., dimethoxyphosphinylamino and dimethylaminophosphinylamino); and silyl group (preferably a substituted or unsubstituted silyl group having 3 to 30 carbon atoms, e.g., trimethylsilyl, t-butyldimethylsilyl, and phenyldimethylsilyl). [0035]

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Of the above substituents, those having a hydrogen atom may be further substituted by the above groups by removing the hydrogen atom. Examples of such substituents are an alkylcarbonylaminosulfonyl group, arylcarbonylaminosulfonyl group, alkylsulfonylaminocarbonyl group, and arylsulfonylaminocarbonyl group. Examples of these groups are methylsulfonylaminocarbonyl, p-methylphenylsulfonylaminocarbonyl, acetylaminosulfonyl, and benzoylaminosulfonyl groups.

[0036]

The structures of the formula (TS-1) are preferably those where R¹ is a hydrogen atom, a substituted or unsubstituted alkyl group having 1 to 30 carbon atoms (including cycloalkyl and bicycloalkyl groups); substituted or unsubstituted alkenyl group having 3 to 30 carbon atoms (including cycloalkenyl and bicycloalkenyl groups); or substituted or unsubstituted aryl group having 6 to 30 carbon atoms.

10 [0037]

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 $-X^{1}$ — is preferably -O-, or $-N(R^{24})$ —, wherein R^{24} is preferably a substituted or unsubstituted alkyl group having 1 to 30 carbon atoms.

[0038]

Preferably, R², R³, R⁴, R⁵ and R⁶ may be the same or different from each other, and each thereof represents a hydrogen atom, a substituted or unsubstituted alkyl group having 1 to 30 carbon atoms, substituted or unsubstituted alkoxy group having 1 to 30 carbon atoms, substituted or unsubstituted acylamino group having 1 to 30 carbon atoms, or a halogen atom. R⁴ is preferably a substituted or unsubstituted alkyl group having 1 to 30 carbon atoms, more preferably, an alkyl group having a total carbon atoms including those of a substituent attached thereto of 4 or more.

[0039]

Among the compounds of the general formula (TS-I),

those represented by the following formulae (TS-I-lpha) and (TS-I-eta) are preferred:

[0040]

[Chem 3]

In the formula (TS-I- α), R², R³, R⁵ and R⁶ each independently have the same meaning as the R², R³, R⁵ and R⁶ of the general formula (TS-I).

10 [0042]

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In the formula $(TS-I-\beta)$, R^{3a} , R^{3b} , R^{4a} , R^{4b} , R^{5a} , R^{5b} , R^{6a} and R^{6b} each independently have the same meaning as the R^3 , R^4 , R^5 and R^6 of the general formula (TS-I). X^{1c} and X^{1d} each independently have the same meaning as the X^1 of the general formula (TS-I). R^{1c} and R^{1d} each independently have the same meaning as the R^1 of the general formula (TS-I). L^4 represents a substituted or unsubstituted alkylene group having 1 to 20 carbon atoms.

20 [0043]

Among the compounds of the formula (TS-I- α), those wherein each of R², R³, R⁵ and R⁶ independently represents a hydrogen atom, a substituted or

unsubstituted alkyl group having 1 to 20 carbon atoms, a halogen atom, a substituted or unsubstituted alkoxy group having 1 to 20 carbon atoms or an acylamino group having 1 to 20 carbon atoms are preferred. Among the preferable groups of R^2 , R^3 , R^5 and R^6 , they independently represent more preferably a hydrogen atom, or a substituted or unsubstituted alkyl group having 1 to 8 carbon atoms.

[0044]

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Of the preferable structure of formula $(TS-I-\alpha)$, R^6 is preferably an unsubstitued tert-alkyl group having 3 to 8 carbon atoms, R^5 is a hydrogen atom, R^4 is a substituted or unsubstituted alkyl group having 1 to 30 carbon atoms, either R^2 or R^3 is a hydrogen atom, and the other is an alkyl group having 1 to 8 carbon atoms.

[0045]

The compound having the structure of the formula (TS-I-β) is preferably those wherein each of R³a, R³b, R⁴a, R⁴b, R⁵a, R⁵b, R⁶a and R⁶b independently represents a hydrogen atom, a substituted or unsubstituted alkyl group having 1 to 20 carbon atoms, a halogen atom or an acylamino group having 1 to 20 carbon atoms. Preferably, each of X¹c and X¹d independently represents -O-. Further, preferably, each of R¹c and R¹d independently represents a hydrogen atom, a substituted or unsubstituted alkyl group having

1 to 20 carbon atoms, an acylamino group having 2 to 20 carbon atoms, or a substituted or unsubstituted alkenyl group having 3 to 20 carbon atoms. L^4 preferably represents an unsubstituted alkylene group having 1 to 20 carbon atoms.

[0046]

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More preferably, R^{1c} and R^{1d} simultaneously represent hydrogen atoms, and R^{3a} , R^{3b} , R^{5a} , and R^{5b} simultaneously represent hydrogen atoms. L^4 more preferably represents an unsubstituted alkylene group having 1 to 8 carbon atoms.

[0047]

More preferable compounds having the structure of formula (TS-I- β) are those in which R⁴a, R⁴b, R⁶a, and R⁶b each independently represent unsubstituted alkyl group having 1 to 8 carbon atoms, all of R¹c, R¹d, R³a, R³b, R⁵a and R⁵b simultaneously represent hydrogen atoms, both of X¹c and X¹d represent -O-, and L⁴ represents an unsubstituted alkylene group having 1 to 8 carbon atoms.

[0048]

Among the compounds of the general formula (TS-II), those wherein each of R^{11} , R^{12} , R^{13} and R^{14} represents an unsubstituted alkyl group having 1 to 10 carbon atoms or an alkenyl group having 2 to 10 carbon atoms are preferred. More preferably, R^{11} , R^{12} , R^{13} and R^{14} are the same and represent an unsubstituted alkyl group

having 1 to 3 carbon atoms. Still more preferably, R^{11} , $_{
m R}^{12}$, $_{
m R}^{13}$ and $_{
m R}^{14}$ simultaneously represent a methyl group. R^{11} and R^{12} , or R^{13} and R^{14} , may be bonded with each other to thereby form a 5- to 7-membered ring. χ^2 preferably represents any of a hydrogen atom, alkyl 5 groups (including cycloalkyl and bicycloalkyl groups), alkenyl groups (including cycloalkenyl and bicycloalkenyl groups), alkoxy groups (including a cycloalkyloxy group), acyl groups, acyloxy groups, a hydroxyl group and oxy radical group. Among them, χ^2 10 more preferably represents an unsubstituted alkoxy group having 1 to 20 carbon atoms (including a cycloalkyloxy group) or an oxy radical group. χ^3 preferably represents an atom group required for forming a nitrogen-containing 6-membered ring, in which 15 the number of the nitrogen atom is preferably 1 to 3, and more preferably 1. The cyclic ring that X^3 forms. together with the nitrogen atom preferably have a substituent, and the position of the substituent is preferably para-position with respect to the nitrogen 20 atom to which X^2 of the general formula (TS-II) attaches.

[0049]

In a preferred form of the general formula (TS-II), R^{11} , R^{12} , R^{13} and R^{14} simultaneously represent a methyl group. X^2 represents an unsubstituted alkoxy group having 1 to 20 carbon atoms (including a cycloalkyloxy

group) or an oxyl radical group. x^3 represents an atom group required for forming a nitrogen-containing 6-membered ring.

[0050]

Among the compounds represented by the general formula (TS-I) or (TS-II), those represented by formula (TS-I) are preferable, and those represented by formula (TS-I- α) are more preferable.

[0051]

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It has been revealed that the larger the molecular weight of the compound represented by the general formula (TS-I) or (TS-II) the more the advantages of the compound are. The molecular weight is preferably 230 or more, more preferable 300 or more. The molecular weight is preferably 1000 or less, more preferably 700 or less, and most preferably 600 or less.

Specific examples of the preventive agent represented by general formula (TS-I) or (TS-II) are set for the below, however the present invention is not limited to those.

S-5.

[0054] [Chem 5] S-6.

$$A$$
 CH_3
 CH_3
 CH_3

S-7.
$$C \leftarrow CH_2 \qquad 0 \\ O-C-CH_2-CH_2 \rightarrow OH$$

[0055] [Chem 6]

S-11.

$$CH_2$$
 CH_2
 CH_2

S-12.

$$H_3C$$
 OH
 CH_3

S-13.

$$CH_2$$
 CH_2 CH_2 CH_2 CH_2 CH_2 CH_2 CH_2 CH_2 CH_2 CH_2

S-14.

$$CH_2-C-N$$
 CH_2
 CH_2

[0056] [Chem 7]

S-15.

S-16.

S-17.

S-18.

$$H_{3}C$$
 $H_{2}C$
 OH
 $S-C_{8}H_{17}$
 $S-C_{8}H_{17}$
 $S-C_{8}H_{17}$

S-19.

$$CH_2$$
 CH_2 CH_2 CH_2 CH_2 CH_2 CH_2 CH_2

[0057] [Chem 8]

[0058]

Compounds of the general formulae (TS-I) and (TS-II) are known, and relevant patents are cited in, for example, Research Disclosure Nos. 17643 (IV, items I to J), 15162, 18716 (page 650, left column), 36544 (page 527), 307105 (page 872) and 15162.

[0059]

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These compounds are sold as industrial products on the market and hence can be easily procured. With respect to those which are commercially available, detailed description is given in "The index of ANTIOXIDANTS and ANTIOZONANTS" edited by Michael and Irene Ash and published by Gower.

[0060]

All the compounds listed as compound examples are sold as industrial products on the market and can be procured from a plurality of companies. Representative sources and trade names are listed below.

[0061]

20	S-1.	MARK AO-50	Adeka Argus Chemical Co., Ltd.
		IRGANOX 1076	Ciba Specialty Chemical
	S-2.	MARK AO-20	Adeka Argus Chemical Co., Ltd.
	S-3.	MARK AO-30	Adeka Argus Chemical Co., Ltd.
	S-4.	MARK AO-40	Adeka Argus Chemical Co., Ltd.
25	S-5.	MARK AO-80	Adeka Argus Chemical Co., Ltd.
	S-6.	MARK AO-330	Adeka Argus Chemical Co., Ltd.
	S-7.	SONGLIZER 1010	Morisawa Shoji

	S-8. Sumilizer MDP-S	Sumitomo Chemical Co., Ltd.
	S-9. Sumilizer GM	Sumitomo Chemical Co., Ltd.
	S-10. Sumilizer BBM-S	Sumitomo Chemical Co., Ltd.
	S-11. Tominox 917	Yoshitomi Fine Chemical
5	S-12. Sumilizer WX-R	Sumitomo Chemical Co., Ltd.
	S-13. IRGANOX 1035	Ciba Specialty Chemical
	S-14. IRGANOX 1098	Ciba Specialty Chemical
	S-15. IRGANOX 1141	Ciba Specialty Chemical
	S-16. IRGANOX 1222	Ciba Specialty Chemical
10	S-17. IRGANOX 1425WL	Ciba Specialty Chemical
	S-18. IRGANOX 1520LR	Ciba Specialty Chemical
	S-19. IRGANOX 259	Ciba Specialty Chemical
	S-20. TINUVIN 123-S	Ciba Specialty Chemical
	S-21. TINUVIN 144	Ciba Specialty Chemical
15	S-22. TINUVIN 765	Ciba Specialty Chemical
	S-23. MARK LA-77	Adeka Argus Chemical Co., Ltd.
	S-24. MARK LA-67	Adeka Argus Chemical Co., Ltd.
	S-25. MARK LA-31	Adeka Argus Chemical Co., Ltd.
	S-26. Sumilizer BHT	Sumitomo Chemical Co., Ltd.
20	[0062]	
	The addition amount	t

The addition amount of compounds represented by the general formulae (TS-I) and (TS-II) according to the present invention is in the range of 0.0005 to 5.0% by weight, preferably 0.001 to 3.0% by weight, and more preferably 0.002 to 1.0% by weight. Herein, the addition amount refers to the total usage in plastic material.

[0063]

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The substance capable of adsorbing substances having adverse effects on photographic properties according to the present invention will be described in detail below.

The aforementioned gases are known as substances having adverse effects on photographic properties, and carbon black, alumina, titanium oxide and high-silica zeolite (produced by Union Showa K.K., trade name: deodorant Abscents 3000) can preferably be employed as adsorbents of such gases. It has been found that, especially, carbon blacks has excellent adsorbing performance to such various gases, which is preferable.

[0064]

I has bee found that among the carbon blacks, specific carbon blacks which are defined by an equilibrium adsorption amount of acetaldehyde gas. Specifically, carbon blacks having the acetaldehyde gas equilibrium adsorption amount of carbon black of 2 mg/g or more are preferable, and those of 3 mg/g or more are more preferable.

In order for the carbon blacks to have such an adsorbing performance, those having a smaller average grain diameters and porous are preferred. Preferably, the average grain diameter is 30 nm or less, more preferably the average grain diameter is 20 nm or less.

[0065]

The acetaldehyde gas equilibrium adsorption amount mentioned in the present invention is measured in the following manner.

2.5 to 3.5 g of carbon black is weighed and charged in a glass tube (20 mm in inside diameter and 20 mm in length). In a 25° C atmosphere, an air containing acetaldehyde gas in a concentration of 100 ppm (hereinafter referred to as "mixed gas") is passed through the glass tube charged with carbon black at a gas flow rate of 0.417 normal liter/min (the normal liter refers to a volume in terms of 1 atm and gas having passed through the glass tube charged with carbon black is measured by means of an acetaldehyde gas detector tube (No. 92, manufactured by Gastec Corporation) until the acetaldehyde gas concentration comes to agree with the acetaldehyde gas concentration (100 ppm) of the mixed gas before being passed through the glass tube. The amount of acetaldehyde gas having been adsorbed up to the time at which the acetaldehyde gas concentrations agree with each other is referred to as "acetaldehyde gas equilibrium adsorption amount".

[0066]

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The carbon blacks used in the present invention is contained, as a dispersed state, in the total resin in an amount within the range of 0.05 to 15% by weight.

Herein, the terminology "contain" refers to the total

amount after the supplemental addition to the plastic material.

As an example of commercially available carbon black preferred in the present invention, Furnace Carbon Black #950 and #2600 produced by Mitsubishi Chemical Corporation can be mentioned.

[0067]

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The photographic lightsensitive material member and container using the reclaimed resin according to the present invention are not limited to those accommodated together with a lightsensitive material, such as a body of a lens-fitted package unit, a spool and a core of 35 mm patrone, but include those used in a container material such as a photographic film case. Also, members and containers using the reclaimed resin according to the present invention may use a member constituted of other materials (e.g., a metal) in combination.

[0068]

The thermo plastic reclaimed resin used in the present invention is not limited to a known resin such as polyethylene-based resin, ABS resin and polypropylene resin. However, polystyrene resin is preferable in view of cost and thermal stability.

The reclaimed resin of the present invention may contain the same resin as the base material in order to bring the resin property changed by the supplementally

added substance back to the original resin property, or contain a different kind of resin solely or a plurality of different kinds of resins as long as the different kid of resin is miscible to the reclaimed resin.

5 [0069]

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A method of supplementally adding a substance adsorbing a substance giving an adverse effect on photographic properties or a compound suppressing the generation thereof may be one in which it, in the form of fine powder, is supplied together with a dispersant and mixed, or may be one in which it, with a high content, is kneed into a resin to prepare a master batch and then mixed with the reclaimed resin. The master batch method is preferable in view of good workability and little contamination to the surrounding.

[0070]

The point at which the substance or compound is supplementally added is not limited and includes at the time of pelleting through extruding a crushed resin with an extruder, at the time of molding the pelletized resin alone or after mixing it with another resin, or at the time of molding the crushed resin as it is or after mixing it with another resin in the form of pellets. Further a molding method is not limited and includes injection molding, as well as vacuum molding, blow molding, and extrusion molding. An extrusion method is not particularly limited.

[0071]

The reclaimed resin of the present invention may contain additives, for example, various silicone oils added for low friction, fatty acid metal salts for mold release improvement and surfactants for antistatic properties.

Details of applicable resins, adsorbents, additives, etc. are given in JP-A-6-67356, which however in no way limit the present invention.

10 [0072]

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The color photographic lightsensitive material of the present invention has, on a support, a redsensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a blue-sensitive silver halide emulsion layer. photographic speed of the lightsensitive material of the present invention is preferably 640 or more in terms of ISO. The use of conventional reclaimed resin has caused the lightsensitive material of 640 or more ISO speed to suffer adverse effects on photographic properties, thereby disenabling practical photographing. However, the supplemental addition, at reclamation, of the substance capable of adsorbing substances having adverse effects on photographic properties or the compound suppressing the same has enabled employing reclaimed resin members for the lightsensitive material of 640 or more ISO speed.

[0073]

With respect to the ISO speed of the color photographic lightsensitive material of the present invention, a distance effect is striking when it is 800 or more.

[0074]

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The silver content of the color photographic lightsensitive material of the present invention is preferably in the range of 6 to 10 g/m^2 , more preferably 6 to 9 g/m^2 . The terminology "silver 10 content" used herein means the total amount, in terms of silver, of contained silvers such as silver halides and metallic silver. Some methods are known for ' analyzing the silver content of lightsensitive material. Although any of the methods can be employed, for 15 example, the elemental analysis using fluorescent X-ray technique is easy to apply. It has been found that the substances having adverse effects on photographic properties affect silver halides. Therefore, the present invention has enabled employing reclaimed resin 20 members for the lightsensitive material of large silver coating amount as well.

[0075]

The film thickness of color photographic

lightsensitive material mentioned in the present invention refers to the sum of all thicknesses of hydrophilic colloid layers arranged on the support on

its side of lightsensitive silver halide emulsion layers. The film thickness is preferably 22 μm or more, more preferably in the range of 23 to 27 μm .

The film thickness is measured by effecting a magnified photographing of a section of lightsensitive material by means of a scanning electron microscope.

[0076]

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An exploded figure of a lens-fitted lightsensitive material package unit of the present invention is shown in Fig. 1. On both ends of body base 3, patrone chamber 10 fitting 135-size patrone 12 and film role chamber 11 are combined and assembled. During the production, a 135-size patrone 12 and a film roll of a photographic film 13 that was pulled out of this 135-size patrone 12 and being in rolled state are loaded in patrone chamber 10 and film role chamber 11, respectively.

[0077]

lt was found out that in a lightsensitive material loaded, as a rolled state, in film roll chamber 11 of a lens-fitted lightsensitive material package unit using a reclaimed resin, the larger the film thickness is the more conspicuous the phenomenon of uneven fogging found. When a lightsensitive material having a film thickness of less than 22 μ m, the same fogging phenomenon was observed. However, the fogging was not uneven but even. The phenomenon of fogging is of course not preferable.

However, when the fogging is even, the influence on the finishing of a photography may be suppressed by compensating tint of a printer. Contrary to this, uneven fogging is not preferable for a lightsensitive material because such compensation as mentioned above can not be conducted.

[0078]

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The present invention can provide a lens-fitted lightsensitive material package unit without any influence on photographic properties for a lightsensitive material having a film thickness of 22 μ m.

[0079]

In the present invention, it was revealed that a reclaimed resin may be used as a member material in a lightsensitive material having severe conditions of an ISO speed of ISO 640 or more, a silver content of 6 to $10~\rm g/m^2$, and a film thickness of 22 $\mu\rm m$ or more.

[0080]

20 This industry has a fierce competition for enhancing speed of a silver halide lightsensitive material for regular use. ISO 400 has been widely used as a lightsensitive material for regular use. It is a big problem for environment, accompanying the more enhancement in speed of the regular use film, that a reclaimed resin can not be used as a material member to be used therein. It has been revealed that the present

invention enabled the use of a reclaimed resin also for a high speed lightsensitive material.

[0081]

The emulsions capable of using in the lightsensitive material of the present invention is preferably silver iodobromide or silver chloroiodobromide grain emulsion.

Grain shape of the silver halide grains in the present invention is not particularly limited and includes regular crystal such as cubic, octahedral or tetradecahedral, or tabular grains having (111) faces as main planes, tabular grains composed of (100) faces of main planes, or grains having an epitaxial. However, tabular grains are preferable.

15 [0082]

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With respect to the tabular silver halide grains (hereinafter also simply referred to as "tabular grains"), the terminology "aspect ratio" means the ratio of diameter to thickness of the silver halide. That is, it is a quotient of the diameter divided by the thickness of each individual silver halide grain. The terminology "diameter" used herein refers to the diameter of a circle having an area equal to the projected area of grain as obtained when observing silver halide grains through a microscope or an electron microscope.

[0083]

The color photographic lightsensitive material of the present invention has at least one each of a redsensitive silver halide emulsion layer, a greensensitive silver halide emulsion layer and a bluesensitive silver halide emulsion layer, on a support. 5 It is preferred that each color-sensitive silver halide emulsion be in the form of a plurality of silver halide emulsion layers differing from each other in photographic speed, and 50% or more of the total projected area of silver halide grains contained in at 10 least two of the emulsion layers each having a highest speed is occupied by tabular silver halide grains having an average aspect ratio of 8 or more. average aspect ratio is more preferably 10 or more, and most preferably 12 or more. The upper limit of the 15 aspect ratio is preferably 20.

[0084]

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The average aspect ratio in the present invention means an average value of all the tabular grains in an emulsion.

The method of taking a transmission electron micrograph by the replica technique and measuring the equivalent circular diameter and thickness of each individual grain can be mentioned as an example of aspect ratio determining method. In the mentioned method, the thickness is calculated from the length of replica shadow.

[0085]

The configuration of tabular grains of the present invention is generally hexagonal. The terminology "hexagonal configuration" means that the shape of the principal plane of tabular grains is hexagonal, the 5 neighboring side ratio (maximum side length/minimum side length) thereof being 2 or less. The neighboring side ratio is preferably 1.6 or less, more preferably 1.2 or less. That the lower limit thereof is 1.0 is needless to mention. In the grains of high aspect 10 ratio, especially, triangular tabular grains are increased in the tabular grains. The triangular tabular grains are produced when the Ostwald ripening has excessively been advanced. From the viewpoint of .15 obtaining substantially hexagonal tabular grains, it is preferred that the period of this ripening be minimized. For this purpose, it is requisite to endeavor to raise the tabular grain ratio by nucleation. It is preferred that one or both of an aqueous silver ion solution and an aqueous bromide ion solution contain gelatin for the 20 purpose of raising the probability of occurrence of hexagonal tabular grains at the time of adding silver ions and bromide ions to a reaction mixture according to the double jet technique, as described in 25 JP-A-63-11928 by Saito.

[0086]

The hexagonal tabular grains for use in the

present invention are formed through the steps of nucleation, Ostwald ripening and growth. Although all of these steps are important for suppressing the spread of grain size distribution, especial attention should 5 be paid so as to prevent the spread of size distribution at the first nucleation step because the spread of size distribution brought about in a previous step cannot be narrowed by an ensuing step. What is important in the nucleation step is the relationship 10 between the temperature of reaction mixture and the period of nucleation comprising adding silver ions and bromide ions to a reaction mixture according to the double jet technique and producing precipitates. JP-A-63-92942 by Saito describes that it is preferred that the temperature of the reaction mixture at the time of nucleation be in the range of from 20 to 45%for realizing a monodispersity enhancement. Further, JP-A-2-222940 by Zola et al describes that the suitable temperature at nucleation is 60° C or below.

20 [0087]

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Gelatin may be further added during the grain formation in order to obtain monodisperse tabular grains of high aspect ratio. The added gelatin preferably consists of a chemically modified gelatin as described in JP-A-10-148897 and JP-A-11-143002 (gelatin in which at least two -COOH groups have newly been introduced at a chemical modification of $-NH_2$ group

contained in the gelatin). Although this chemically modified gelatin is a gelatin characterized in that at least two carboxyl groups have newly been introduced at a chemical modification of amino group contained in the gelatin, it is preferred that gelatin trimellitate be used as the same. Also, gelatin succinate is preferably used. The chemically modified gelatin is preferably added prior to the growth step, more preferably immediately after the nucleation. The addition amount thereof is preferably at least 60%, more preferably at least 80%, and most preferably at least 90%, based on the total weight of dispersion medium used in grain formation.

[8800]

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The tabular grain emulsion is preferably 15 constituted of silver iodobromide or silver chloroiodobromide. Although silver chloride may be contained, the silver chloride content is preferably 8 mol% or less, more preferably 3 mol% or less, or 20 The silver iodide content is preferably 0 mol%. 20 mol% or less since the variation coefficient of the grain size distribution of the tabular grain emulsion is preferably 30% or less. The lowering of the variation coefficient of the distribution of equivalent circular diameter of the tabular grain emulsion can be 25 facilitated by lowering the silver iodide content. variation coefficient of the grain size distribution of

the tabular grain emulsion is more preferably 20% or less, and the silver iodide content is more preferably 10 mol% or less.

[0089]

It is preferred that the tabular grain emulsion have some intragranular structure with respect to the silver iodide distribution. The silver iodide distribution may have a double structure, a treble structure, a quadruple structure or a structure of higher order.

[0090]

In the present invention, the tabular grains preferably have dislocation lines. The dislocation lines of the tabular grains can be observed by 15 the direct method using a transmission electron microscope at low temperatures as described in, for example, J. F. Hamilton, Phot. Sci. Eng., 11, 57 (1967) and T. Shiozawa, J. Soc. Phot. Sci. Japan, 3, 5, 213 (1972). Illustratively, silver halide grains are 20 harvested from the emulsion with the care that the grains are not pressurized with such a force that dislocation lines occur on the grains, are put on a mesh for electron microscope observation and, while cooling the specimen so as to prevent damaging 25 (printout, etc.) by electron beams, are observed by the transmission method. The greater the thickness of the above grains, the more difficult the transmission

of electron beams. Therefore, the use of an electron microscope of high voltage type (at least 200 kV on the grains of 0.25 μm in thickness) is preferred for ensuring clearer observation. The thus obtained photograph of grains enables determining the position and number of dislocation lines in each grain viewed in the direction perpendicular to the principal planes.

[0091]

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The number of dislocation lines of the tabular grains according to the present invention is preferably 10 at least 10 per grain on the average and more preferably at least 20 per grain on the average. When dislocation lines are densely present or when dislocation lines are observed in the state of crossing 15 each other, it happens that the number of dislocation lines per grain cannot accurately be counted. However, in this instance as well, rough counting on the order of, for example, 10, 20 or 30 dislocation lines can be effected, so that a clear distinction can be made from the presence of only a few dislocation lines. 20 The average number of dislocation lines per grain is determined by counting the number of dislocation lines of each of at least 100 grains and calculating a number average thereof. There are instances when hundreds of 25 dislocation lines are observed.

[0092]

Dislocation lines can be introduced in, for

example, the vicinity of the periphery of tabular grains. In this instance, the dislocation is nearly perpendicular to the periphery, and each dislocation line extends from a position corresponding to x% of the distance from the center of tabular grains to the side (periphery) to the periphery. The value of xpreferably ranges from 10 to less than 100, more preferably from 30 to less than 99, and most preferably from 50 to less than 98. In this instance, the figure created by binding the positions from which the dislocation lines start is nearly similar to the configuration of the grain. The created figure may be one which is not a complete similar figure but deviated. The dislocation lines of this type are not observed around the center of the grain. The dislocation lines are crystallographically oriented approximately in the (211) direction. However, the dislocation lines often meander and may also cross each other.

20 [0093]

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Dislocation lines may be positioned either nearly uniformly over the entire zone of the periphery of the tabular grains or local points of the periphery. That is, referring to, for example, hexagonal tabular silver halide grains, dislocation lines may be localized either only in the vicinity of six apexes or only in the vicinity of one of the apexes. Contrarily,

dislocation lines can be localized only in the sides excluding the vicinity of six apexes.

[0094]

Furthermore, dislocation lines may be formed over 5 regions including the centers of two mutually parallel principal planes of tabular grains. In the case where dislocation lines are formed over the entire regions of the principal planes, the dislocation lines may crystallographically be oriented approximately in the (211) direction when viewed in the direction perpendicular to the principal planes, and the formation of the dislocation lines may be effected either in the (110) direction or randomly. Further, the length of each dislocation line may be random, and the dislocation lines may be observed as short lines on the principal planes or as long lines extending to the side (periphery). The dislocation lines may be straight or often meander. In many instances, the dislocation lines cross each other.

20 [0095]

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The position of dislocation lines may be localized on the periphery, principal planes or local points as mentioned above, or the formation of dislocation lines may be effected on a combination thereof. That is, dislocation lines may be concurrently present on both the periphery and the principal planes.

[0096]

For thhe introduction of dislocation lines in the tabular grains can be accomplished by a method of adding aqueous solutions of silver ions and iodide ions by the double jet method to form a silver halide layer containing silver iodide as disclosed in JP-A-63-220238; a method of adding silver iodide fine grains abruptly followed by forming a shell as described in JP-A-11-15088; or a method of forming a silver halide layer containing silver iodide while adding iodide ions abruptly by using an iodide ion-releasing agent as disclosed in US Patent No. 5,496,694; a method of introducing dislocation line selectively at a specific portion of silver halide grains as disclosed in JP-A-4-14951, and JP-A-9-189974; a method of forming a silver halide layer containing silver iodide while preparing fine silver halide gains containing 95 mol% or more of silver iodide in a mixer provided outside the reaction vessel, and adding them.

[0097]

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The variation coefficient of the intergranular iodine distribution of silver halide grains for use in the present invention is preferably 20% or less, more preferably 15% or less, and much more preferably 10% or less. When the variation coefficient of the iodine content distribution of each silver halide is greater than 20%, unfavorably, a high contrast is not realized and a sensitivity lowering is intense when a pressure

is applied.

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[0098]

During any production steps of the silver halide emulsion to be used in the present invention, at least 5 one of chalcogen sensitization such as sulfur sensitization, selenium sensitization and tellurium sensitization, and noble metal sensitization such as gold sensitization and palladium sensitization, and reduction sensitization may be performed. preferable to combine tow kinds or more sensitization methods. Various types of emulsions may be prepared by selecting the step at which the chemical sensitization is performed. There are types such as impregnating chemical sensitization nuclei inside the grains, impregnating chemical sensitization nuclei at shallow position from the grain surfaces, or making chemical sensitization nuclei on the surfaces. Although the position of the chemical sensitization nuclei may be selected depending on purposes in the emulsion of the present invention, the case in which at least one kind of chemical sensitization nuclei is made near the surfaces, is generally preferred.

[0099]

One chemical sensitization which can be preferably

performed in the present invention is chalcogen
sensitization, noble metal sensitization, or a
combination of these. The sensitization can be

performed by using active gelatin as described in T. H. James, The Theory of the Photographic Process, 4th ed., Macmillan, 1977, pages 67 to 76. The sensitization can also be performed by using any of sulfur, selenium, 5 tellurium, gold, platinum, palladium, and iridium, or by using a combination of a plurality of these sensitizers at pAg 5 to 10, pH 5 to 8, and a temperature of 30 to 80°C , as described in Research Disclosure, Vol. 120, April, 1974, 12008, Research Disclosure, Vol. 34, June, 1975, 13452, U.S.P.'s 10 2,642,361, 3,297,446, 3,772,031, 3,857,711, 3,901,714, 4,266,018 and 3,904,415 and British Patent 1,315,755. In the noble metal sensitization, salts of noble metals, such as gold, platinum, palladium, and iridium, can be 15 In particular, gold sensitization, palladium used. sensitization, or a combination of the both is preferred.

[0100]

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The emulsions for use in the silver halide
20 lightsensitive material of the present invention are
preferably subjected to selenium sensitization.

Selenium compounds disclosed in hitherto published patents can be used as the selenium sensitizer in the present invention. In the use of labile selenium compound and/or nonlabile selenium compound, generally, it is added to an emulsion and the emulsion is agitated at high temperature,

Compounds described in, for example, Jpn. Pat. Appln. KOKOKU Publication No. (hereinafter referred to as JP-B-) 44-15748, JP-B-43-13489, JP-A's-4-25832 and 4-109240 are preferably used as the labile selenium compound. The addition amount of the selenium sensitizer used in the present invention varies depending on an activity of a used selenium sensitizer, a kind and size of silver halide, a ripening temperature and time, but is preferably 2 \times 10⁻⁶ mol to 5 \times 10⁻⁶ mol per mol of silver halide. The temperature of chemical sensitization using a selenium pAg and pH are arbitral. For example, the advantages of the present invention may be obtained in a wade range of pH from 4 to 9.

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The emulsion for use in the present invention is preferably subjected to gold sensitization in combination. The oxidation number of gold of the gold sensitizer used in the gold sensitization may be either +1 or +3, and gold compounds customarily used as gold sensitizers can be employed. Representative examples thereof include chloroauric acid salts, potassium chloroaurate, auric trichloride, potassium auric thiocyanate, potassium iodoaurate, tetracyanoauric acid, ammonium aurothiocyanate, pyridyltrichlorogold, gold sulfide and gold selenide. The addition amount of gold

sensitizer, although varied depending on various conditions, is preferably between 1 \times 10⁻⁷ mol and 5 \times 10⁻⁵ mol per mol of silver halide as a yardstick.

[0101]

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With respect to the emulsion for use in the present invention, it is desired to perform sulfur sensitization among the chemical sensitization.

In the above sulfur sensitization, those known as sulfur sensitizers can be used. For example, use can be made of thiosulfates, allylthiocarbamidothiourea, allyl isothiacyanate, cystine, p-toluenethiosulfonates and rhodanine. Use can also be made of other sulfur sensitizers described in, for example, U.S.P. Nos. 1,574,944, 2,410,689, 2,278,947, 2,728,668, 3,501,313, and 3,656,955, and

DE No. 1,422,869, JP-B-56-24937 and JP-A-55-45016. The addition amount of sulfur sensitizer is satisfactory if it is sufficient to effectively increase the sensitivity of the emulsion. This amount, although varied to a large extent under various conditions such as the pH, temperature and size of silver halide grains, is preferably in the range of 1×10^{-7} to 5×10^{-5} mol per mol of silver halide.

[0102]

The silver halide emulsion to be used in the present invention can be subjected to a reduction sensitization during the grain formation, or after the

grain formation but before the chemical sensitization, during the chemical sensitization or after the chemical sensitization.

[0103]

The reduction sensitization can be performed by a method selected from among the method in which a reduction sensitizer is added to the silver halide emulsion, the method commonly known as silver ripening in which growth or ripening is carried out in an environment of pAg as low as 1 to 7 and the method commonly known as high-pH ripening in which growth or ripening is carried out in an environment of pH as high as 8 to 11. At least two of these methods can be used in combination.

15 [0104]

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The above method in which a reduction sensitizer is added is preferred from the viewpoint that the level of reduction sensitization can be finely regulated.

Examples of known reduction sensitizers include stannous salts, ascorbic acid and derivatives thereof, amines and polyamines, hydrazine derivatives, formamidinesulfinic acid, silane compounds and borane compounds. In the reduction sensitization according to the present invention, appropriate one may be selected from among these known reduction sensitizers and used or at least two may be selected and used in combination. Preferred reduction

sensitizers are stannous chloride, thiourea dioxide, dimethylaminoborane, ascorbic acid and derivatives thereof. Although the addition amount of reduction sensitizer must be selected because it depends on the emulsion manufacturing conditions, it is preferred that the addition amount range from 10^{-7} to 10^{-3} mol per mol of silver halide.

[0105]

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An oxidizer capable of oxidizing silver is preferably used during the process of producing the 10 emulsion for use in the lightsensitive material of the present invention. The silver oxidizer is a compound having an effect of acting on metallic silver to thereby convert the same to silver ion. A particularly effective compound is one that converts very fine 15 silver grains, formed as a by-product in the step of forming silver halide grains and the step of chemical sensitization, into silver ions. Each silver ion produced may form a silver salt sparingly soluble in 20 water, such as a silver halide, silver sulfide or silver selenide, or may form a silver salt easily soluble in water, such as silver nitrate. The silver oxidizer may be either an inorganic or an organic substance.

25 [0106]

Examples of suitable inorganic oxidizers include ozone, hydrogen peroxide and its adducts

(e.g., NaBO2·H2O2·3H2O, 2NaCO3·3H2O2, Na4P2O7·2H2O2 and 2Na2SO4·H2O2·2H2O), peroxy acid salts (e.g., $K_2S_2O_8$, $K_2C_2O_6$ and $K_2P_2O_8$), peroxy complex compounds (e.g., $K_2[Ti(O_2)C_2O_4]\cdot 3H_2O$, $4K_2SO_4\cdot Ti(O_2)OH\cdot SO_4\cdot 2H_2O$ and Na3[VO(O2)(C2H4)2]·6H2O), permanganates (e.g., $KMnO_4$), chromates (e.g., $K_2Cr_2O_7$) and other oxyacid salts, halogen elements such as iodine and bromine, perhalogenates (e.g., potassium periodate), salts of high-valence metals (e.g., potassium hexacyanoferrate (II)) and thiosulfonates.

[0107]

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Examples of suitable organic oxidizers include quinones such as p-quinone, organic peroxides such as peracetic acid and perbenzoic acid and active halogen-releasing compounds (e.g., N-bromosuccinimide, chloramine T and chloramine B).

Oxidizers preferred in the present invention are inorganic oxidizers selected from among ozone, hydrogen peroxide and its adducts, halogen elements and thiosulfonates and organic oxidizers selected from among quinones.

[0108]

The use of the silver oxidizer in combination with the above reduction sensitization is preferred.

This combined use can be effected by performing the reduction sensitization after the use of the oxidizer or vice versa or by simultaneously performing the

reduction sensitization and the use of the oxidizer. These methods can be performed during the step of grain formation or the step of chemical sensitization.

[0109]

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The emulsion for use in the present invention can effectively exhibit it advantages by subjecting it to a spectral sensitization with a methine dye or the like. Examples of employed dyes include cyanine dyes, merocyanine dyes, composite cyanine dyes, composite merocyanine dyes, holopolar cyanine dyes, hemicyanine 10 dyes, styryl dyes and hemioxonol dyes. Particularly useful dyes are those belonging to cyanine dyes, merocyanine dyes and composite merocyanine dyes. dyes may contain any of nuclei commonly used in cyanine 15 dyes as basic heterocyclic nuclei. Examples of such nuclei include a pyrroline nucleus, an oxazoline nucleus, a thiazoline nucleus, a pyrrole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus, an imidazole nucleus, a tetrazole nucleus and a pyridine nucleus; nuclei comprising these nuclei 20 fused with alicyclic hydrocarbon rings; and nuclei comprising these nuclei fused with aromatic hydrocarbon rings, such as an indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxazole nucleus, a

naphthoxazole nucleus, a benzothiazole nucleus, a

benzimidazole nucleus and a quinoline nucleus.

naphthothiazole nucleus, a benzoselenazole nucleus, a

nuclei may have substituents on carbon atoms thereof. [0110]

The merocyanine dye or composite merocyanine dye may have a 5- or 6-membered heterocyclic nucleus such as a pyrazolin-5-one nucleus, a thiohydantoin nucleus, a 2-thioxazolidine-2,4-dione nucleus, a thiazolidine-2,4-dione nucleus, a rhodanine nucleus or a thiobarbituric acid nucleus as a nucleus having a ketomethylene structure.

10 [0111]

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These spectral sensitizing dyes may be used either individually or in combination. The spectral sensitizing dyes are often used in combination for the purpose of attaining supersensitization.

Representative examples thereof are described in U.S.P. Nos. 2,688,545, 2,977,229, 3,397,060, 3,522,052, 3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,672,898, 3,679,428, 3,703,377, 3,769,301, 3,814,609, 3,837,862, and 4,026,707, GB Nos. 1,344,281 and 1,507,803, JP-B's-43-4936 and 53-12375, and JP-A's-52-110618

[0112]

and 52-109925.

The emulsion used in the present invention may contain with a dye which itself exerts no spectral sensitizing effect or a substance which absorbs substantially none of visible radiation and exhibits supersensitization, together with the above spectral

sensitizing dye.

[0113]

The addition timing of the spectral sensitizing dye to the emulsion may be performed at any stage of 5 the process for preparing the emulsion which is known as being useful. Although the doping is most usually conducted at a stage between the completion of the chemical sensitization and the coating, the spectral sensitizing dye can be added simultaneously with the 10 chemical sensitizer to thereby simultaneously effect the spectral sensitization and the chemical sensitization as described in U.S.P. Nos. 3,628,969 and 4,225,666. Alternatively, the spectral sensitization can be conducted prior to the chemical sensitization and, also, the spectral sensitizing dye can be added 15 prior to the completion of silver halide grain precipitation to thereby initiate the spectral sensitization as described in JP-A-58-113928. the above sensitizing dye can be divided prior to 20 addition, that is, part of the sensitizing dye can be added prior to the chemical sensitization with the rest of the sensitizing dye added after the chemical sensitization as taught in U.S.P. No. 4,225,666. Still further, the spectral sensitizing dye can be 25 added at any stage during the formation of silver halide grains according to the method disclosed in U.S.P. No. 4,183,756 and other methods.

[0114]

Although the sensitizing dye can be used in an amount of 4 \times 10⁻⁶ to 8 \times 10⁻³ mol per mol of silver halide contained in the addition layer, the use thereof in an amount of about 5 \times 10⁻⁵ to 2 \times 10⁻³ mol per mol of silver halide is more effective when the size of silver halide grains is in the preferred range of 0.2 to 1.2 μ m.

[0115]

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10 The fogging during aging of the silver halide emulsion for use in the present invention can be improved by adding and dissolving a previously prepared silver iodobromide emulsion at the time of chemical sensitization. Although the timing of the addition is 15 arbitrary as long as it is performed during chemical sensitization, it is preferred that the silver iodobromide emulsion be first added and dissolved and, thereafter, a sensitizing dye and a chemical sensitizer be added in this order. The employed silver iodobromide emulsion has an iodine content lower 20 than the surface iodine content of host grains, which is preferably a pure silver bromide emulsion. This silver iodobromide emulsion, although the size thereof is not limited as long as it is completely dissolvable, preferably has an equivalent spherical 25 diameter of 0.1 $\mu \mathrm{m}$ or less, more preferably 0.05 $\mu \mathrm{m}$ or less. Although the addition amount of silver

iodobromide emulsion depends on employed host grains, basically, it preferably ranges from 0.005 to 5 mol%, more preferably from 0.1 to 1 mol%, based on the mole of silver.

5 [0116]

In the lightsensitive material of the present invention, at least one red-sensitive, at least one green-sensitive and at least one blue-sensitive lightsensitive layer be formed on a support. Each of the color-sensitive layer is constituted by a plurality 10 of silver halide emulsion layers which have substantially the same color sensitivity but have different speeds. In a silver halide color photographic lightsensitive material of the present 15 invention, these unit lightsensitive layers are generally arranged in the order of red-, green- and blue-sensitive layers from a support side. However, according to the intended use, this arrangement order may be reversed, or an arrangement order can be 20 employed in which a different lightsensitive layer is interposed between the layers of the same color sensitivity. Nonlightsensitive layers can be formed between the silver halide lightsensitive layers and as the uppermost layer and the lowermost 25 layer. These may contain, e.g., couplers, DIR compounds and color mixing inhibitors described later. As a plurality of silver halide emulsion lavers

constituting each unit lightsensitive layer, a two-layered structure of high- and low-speed emulsion layers is preferably arranged so that the sensitivity is sequentially decreased toward a support as described in DE No. 1,121,470 or GB No. 923,045.

Also, as described in JP-A's-57-112751, 62-200350, 62-206541 and 62-206543, layers can be arranged so that a low-speed emulsion layer is formed on a side apart from a support while a high-speed emulsion layer is formed on a side close to the support.

[0117]

Specifically, layers can be arranged, from the farthest side from a support, in the order of low-speed blue-sensitive layer (BL)/high-speed blue-sensitive layer (BH)/high-speed green-sensitive layer (GH)/low-speed green-sensitive layer (GL)/high-speed red-sensitive layer (RH)/low-speed red-sensitive layer (RH)/low-speed red-sensitive layer (RL), the order of BH/BL/GL/GH/RH/RL or the order of BH/BL/GH/GL/RL/RH.

20 [0118]

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In addition, as described in JP-B-55-34932, layers can be arranged, from the farthest side from a support, in the order of blue-sensitive layer/GH/RH/GL/RL. Furthermore, as described in JP-A's-56-25738 and 62-63936, layers can be arranged, from the farthest side from a support, in the order of blue-sensitive layer/GL/RL/GH/RH.

[0119]

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As described in JP-B-49-15495, three layers can be arranged so that a silver halide emulsion layer having the highest sensitivity is arranged as an upper layer, a silver halide emulsion layer having sensitivity lower than that of the upper layer is arranged as an interlayer, and a silver halide emulsion layer having sensitivity lower than that of the interlayer is arranged as a lower layer; i.e., three layers having different sensitivities can be arranged so that the sensitivity is sequentially decreased toward the support.

[0120]

Even when a layer structure is constituted by three layers having different sensitivities as mentioned above, these layers can be arranged in the order of medium-speed emulsion layer/high-speed emulsion layer/low-speed emulsion layer from the farthest side from a support in a layer sensitive to one color as described in JP-A-59-202464.

In addition, the order of high-speed emulsion layer/low-speed emulsion layer/medium-speed emulsion layer or low-speed emulsion layer/medium-speed emulsion layer/high-speed emulsion layer can be adopted. Furthermore, the arrangement can be changed as described above even when four or more layers are formed.

[0121]

When the silver halide photographic lightsensitive material of the present invention has at least one each of a red-sensitive silver halide emulsion layer 5 containing a cyan coupler, green-sensitive silver halide emulsion layer containing a magenta coupler and blue-sensitive silver halide emulsion layer containing a yellow coupler and a non-lightsensitive layer on a support and has a specific speed of 640 or more, it is 10 preferable that the spectral sensitivity at 580 nm, i.e., $S_{R(580)}$, of the red-sensitive silver halide emulsion layer meets the following relation ship with respect to the spectral sensitivity of the same layer at the wavelength giving the highest sensitivity, i.e., 15 S_{R(max)}:

$$0.6 \le S_{R(max)} - S_{R(580)} \le 0.9$$

Further, the weight-average wavelength of spectral sensitivity distribution of magnitude of interlayer effect exerted on the red-sensitive silver halide emulsion layer (two or more emulsion layers as a whole) from other silver halide emulsion layers at 500 nm to 600 nm (λ_{-R}) satisfy the relationship: 500 nm < $\lambda_{-R} \leq$ 560 nm; the weight-average wavelength of spectral sensitivity distribution of magnitude of the greensensitive emulsion layer (λ_{-R}) (two or more emulsion layer as a whole) satisfies 520 nm < $\lambda_{-R} \leq$ 580 nm;

and λ_G - $\lambda_{-R} \ge 5$ nm is preferable. [0123]

The sensitizing dye and solid disperse dye for use in the above utilization can be those described in JP-A-11-305396. Further, the above specified sensitivity and weight-average sensitivity wavelength of spectral sensitivity distribution of interlayer effect exerted on the red-sensitive silver halide emulsion layer from other layers can be determined by the method described in JP-A-11-305396.

[0124]

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In the silver halide photographic lightsensitive material of the present invention, it is preferred that the respective spectral sensitivities $S_{\mbox{\scriptsize R}}\mbox{\scriptsize (580)}$ and $S_{\mathsf{G}}(580)$ of the red-sensitive layer and green-sensitive . 15 layer simultaneously satisfy the below given relationships. The $S_G(580)$ and $S_R(580)$ are defined as the respective logarithms of inverse number of exposure required for obtaining densities of magenta color minimum density and cyan color minimum density, 20 respectively, plus 1.0 at the respective wavelengths. The $S_G(max)$ and $S_R(max)$ refer to the sensitivities at highest sensitivity wavelength of the green-sensitive layer and red-sensitive layer, respectively. preferred that the spectral sensitivity does not change 25 from underexposure portion through overexposure portion.

$$0.6 \le S_R(max) - S_R(580) \le 0.9,$$

 $0.6 \le S_G(max) - S_G(580) \le 1.1.$

[0125]

The wavelength at which the red-sensitive layer exhibits the highest sensitivity is in the range of 610 to 640 nm, preferably 620 to 640 nm. Furthermore, it is desired that the spectral sensitivity at 650 nm of the red-sensitive layer $S_R(650)$ satisfy the following relationship:

10 $S_R(650) \le S_R(max) - 0.7$,

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wherein the definition of the spectral sensitivity is as mentioned above.

[0126]

The wavelength at which the green-sensitive layer exhibits the highest sensitivity is in the range of 520 to 580 nm, preferably 540 to 565 nm. Furthermore, it is desirable that the spectral sensitivity at 525 nm of the green-sensitive layer $S_G(525)$ satisfy the following relationship:

20 $0.1 \le S_G(max) - S_G(525) \le 0.3.$ [0127]

It is preferable to utilize an interlayer inhibitory effect as means for improving a color reproduction. It is especially preferred that the weight-average wavelength of spectral sensitivity distribution of the green-sensitive silver halide emulsion layer (λ_G) satisfy the relationship: 520 nm <

 $\lambda_G \leq$ 580 nm; the weight-average wavelength of spectral sensitivity distribution of magnitude of interlayer effect exerted on the red-sensitive silver halide emulsion layer from other silver halide emulsion layers at 500 nm to 600 nm (λ_{-R}) satisfy the relationship: 500 nm < λ_{-R} < 560 nm; and λ_G - λ_{-R} is at least 5 nm, preferably at least 10 nm.

[0128]

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For imparting the above interlayer effect to the red-sensitive layer in a specified wavelength region, it is preferred to dispose a separate interlayer effect donor layer containing silver halide grains, subjected to given spectral sensitization. For realizing the spectral sensitivity desired in the present invention, the interlayer sensitivity wavelength of the interlayer effect donor layer is set at 510 to 540 nm.

[0129]

The weight-average wavelength of wavelength distribution of magnitude of interlayer effect exerted on the red-sensitive silver halide emulsion layer at 500 nm to 600 nm from other silver halide emulsion layers (λ_{-R}) can be determined by the method described in JP-A-11-305396. Further, when λ_{-B} is obtained in the similar to the procedure of obtaining λ_{-R} , the interlayer effect provide by the interlayer effect donating layer must meet the condition (formula (2)) described in JP-A-11-305396.

[0130]

Compounds which react with developing agent oxidation products obtained by development to thereby release a development inhibitor or a precursor thereof 5 are used as the material for exerting the interlayer effect. For example, use can be made of DIR (development inhibitor-releasing type) couplers, DIR-hydroquinone and couplers capable of releasing DIR-hydroquinone or a precursor thereof. When the 10 development inhibitor has a high diffusivity, the development inhibiting effect can be exerted irrespective of the position of the donor layer in the interlayered multilayer structure. However, there also occurs a development inhibiting effect in nonintended 15 directions, Therefore, for correcting this, it is preferred that the donor layer be colored (for example, coloring is made in the same color as that of the layer on which undesirable development inhibitor effect is exerted). From the viewpoint that the lightsensitive 20 material of the present invention obtains desirable spectral sensitivity, it is preferred that the donor layer capable of exerting the interlayer effect realize magenta coloring.

[0131]

Although, for example, the size and configuration of silver halide grains for use in the layer capable of exerting an interlayer effect on the red-sensitive

layer are not particularly limited, it is preferred to use so-called tabular grains of high aspect ratio, a monodisperse emulsion having uniform grain size, or silver iodobromide grains having a layered structure of iodide. Further, for extending an exposure latitude, it is preferred to mix a plurality of emulsions whose grain sizes are different from each other.

[0132]

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Although the donor layer capable of exerting the interlayer effect on the red-sensitive layer may be provided by coating on any position on the support, it is preferred that the donor layer be provided by coating at a position which is closer to the support than the blue-sensitive layer and which is more remote from the support than the red-sensitive layer. It is further preferred that the donor layer be positioned closer to the support than the yellow filter layer.

[0133]

It is more preferred that the donor layer capable of exerting the interlayer effect on the red-sensitive layer be provided at a position which is closer to the support than the green-sensitive layer and which is more remote from the support than the red-sensitive layer. The donor layer is most preferably arranged at a position neighboring to a side of the green-sensitive layer close to the support. The terminology

"neighboring" used herein means that an intermediate layer or any other thing is not interposed therebetween.

There may be a plurality of layers capable of exerting the interlayer effect on the red-sensitive layer. These layers may be positioned so that they neighbor to each other or are apart from each other.

[0134]

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The emulsion for use in the lightsensitive 10 material of the present invention may be any of the surface latent image type in which latent images are mainly formed in the surface, the internal latent image type in which latent images are formed in the internal portion of grains and the type in which latent images exist in both the surface and the internal portion 15 of grains. However, it is requisite that the emulsion be a negative type. The emulsion of the internal latent image type may specifically be, for example, a core/shell internal-latent-image type emulsion described in JP-A-63-264740, whose productive process 20 is described in JP-A-59-133542. The thickness of the shell of this emulsion, although varied depending on development processing, etc., is preferably in the range of 3 to 40 nm, more preferably 5 to 20 nm.

25 [0135]

The silver halide emulsion is generally subjected to physical ripening, chemical sensitization and

spectral sensitization before use. Additives employed in these steps are described in RD Nos. 17643, 18716 and 307105. Positions where the description is made are listed in the following table.

5 [0136]

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With respect to the lightsensitive material of the present invention, at least two emulsions which are different from each other in at least one of the characteristics, specifically the grain size, grain size distribution, halogen composition, grain configuration and sensitivity of lightsensitive silver halide emulsion, can be mixed together and used in one layer.

[0137]

It is preferred that silver halide grains 15 having a grain surface fogged as described in U.S.P. No. 4,082,553, silver halide grains having a grain internal portion fogged as described in U.S.P. No. 4,626,498 and JP-A-59-214852 and colloidal silver be used in lightsensitive silver halide emulsion layers 20 and/or substantially nonlightsensitive hydrophilic colloid layers. The expression "silver halide grains having a grain surface or grain internal portion fogged" refers to silver halide grains which can be 25 developed uniformly (nonimagewise) irrespective of the nonexposed or exposed zone of lightsensitive material. The process for producing the grains is described in

U.S.P. No. 4,626,498 and JP-A-59-214852. The silver halides constituting internal nuclei of core/shell silver halide grains having a grain internal portion fogged may have different halogen composition.

5 [0138]

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Any of silver chloride, silver chlorobromide, silver iodobromide and silver chloroiodobromide can be used as the silver halide having a grain surface or grain internal portion fogged. The average grain size of these fogged silver halide grains is preferably in the range of 0.01 to 0.75 μ m, more preferably 0.05 to 0.6 μ m. With respect to grain configuration, regular grains may be used and although a polydisperse emulsion can be used, monodispersity (at least 95% of the weight or number of silver halide grains have grain sizes falling within ± 40% of the average grain size) is preferred.

[0139]

In the present invention, it is preferred to

20 use nonlightsensitive fine grain silver halide.

The expression "nonlightsensitive fine grain silver halide" refers to silver halide fine grains which are not sensitive at the time of imagewise exposure for obtaining dye image and which are substantially not developed at the time of development processing thereof. Those not fogged in advance are preferred. The fine grain silver halide has a silver bromide content of 0

to 100 mol%, and, if necessary, may contain silver chloride and/or silver iodide. Preferably, silver iodide is contained in an amount of 0.5 to 10 mol%. The average grain size (average of equivalent circular diameter of projected area) of fine grain silver halide is preferably in the range of 0.01 to 0.5 μ m, more preferably 0.02 to 0.2 μ m.

[0140]

The fine grain silver halide can be prepared by

the same process as used in the preparation of common
lightsensitive silver halide. It is not needed to
optically sensitize the surface of silver halide grains.

Further, a spectral sensitization thereof is also not
needed. However, it is preferred to add known

stabilizers such as triazole, azaindene,
benzothiazolium and mercapto compounds and zinc
compounds thereto prior to the addition thereof to
a coating liquid. Colloidal silver can be contained in
the fine grain silver halide containing layers.

20 [0141]

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The above various additives can be used in the lightsensitive material according to the present technology, to which other various additives can also be added in conformity with the object.

The additives are described in detail in Research Disclosure Item 17643 (December 1978), Item 18716 (November 1979) and Item 308119 (December 1989).

A summary of the locations where they are described will be listed in the following table.

[0142]

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3		Types of I additives	RD17643	RD18716	RD308119
10	1	Chemical presentivers	page 23	page 648 right column	page 996
	2	Sensitivity- increasing agents		page 648 right column	
15	3	Spectral presentivers, supersensitizers	- 24	page 648, right column to page 649, right column	right column to page 998,
20	4	Brighteners p			page 998 right column
25	5	Antifoggants, stabilizers			
30	6	Light absorbents, filter dyes, ultraviolet absorbents	pages 25 - 26	page 649, right column to page 650, left column	left column to page 1003,
35	7	Stain preventing agents	right	page 650, left to right columns	right column
40	8	Dye image stabilizers	page 25		page 1002, right column
45	9	Film hardeners .	page 26	page 651, left column	page 1004, right column page 1005, left column
	10	Binders	page 26	page 651,	page 1003,

				left column	right column to page 1004, right column
5	11	Plasticizers, lubricants	page 27	page 650, right column	page 1006, left to right columns
10	12	Coating aids, surfactants			page 1005, left column to page 1006, left column
15		Antistatic agents	page 27	page 650, right column	page 1006, right column to page 1007, left column
20	14	Matting agents			page 1008, left column to page 1009, left column.

[0143]

material of the present invention and the emulsion suitable for use in the photographic lightsensitive material and also with respect to layer arrangement and related techniques, silver halide emulsions, dye forming couplers, DIR couplers and other functional couplers, various additives and development processing which can be used in the photographic lightsensitive material, reference can be made to EP 0565096A1 (published on October 13, 1993) and patents cited therein. Individual particulars and the locations where they are described will be listed below.

[0144]

- Layer arrangement: page 61 lines 23 to 35, page 61 line 41 to page 62 line 14,
- 2. Interlayers: page 61 lines 36 to 40,

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- 3. Interlayer effect imparting layers: page 62 lines 15 to 18,
- 4. Silver halide halogen compositions: page 62 lines 21 to 25,
- 5. Silver halide grain crystal habits: page 62 lines 26 to 30,
- 6. Silver halide grain sizes: page 62 lines 31 to 34,
 - 7. Emulsion production methods: page 62 lines 35 to 40,
 - 8. Silver halide grain size distributions: page 62 lines 41 to 42,
 - 9. Tabular grains: page 62 lines 43 to 46,
- 10. Internal structures of grains: page 62 lines 47 to 53,
 - 11. Latent image forming types of emulsions: page 62 line 54 to page 63 to line 5,
- 12. Physical ripening and chemical sensitization of emulsion: page 63 lines 6 to 9,
 - 13. Emulsion mixing: page 63 lines 10 to 13,
 - 14. Fogging emulsions: page 63 lines 14 to 31,
 - 15. Nonlightsensitive emulsions: page 63 lines 32 to 43,
- 25 16. Silver coating amounts: page 63 lines 49 to 50,
 - 17. Formaldehyde scavengers: page 64 lines 54 to 57,
 - 18. Mercapto antifoggants: page 65 lines 1 to 2,

- 19. Fogging agent, etc.-releasing agents: page 65
 lines 3 to 7,
- 20. Dyes: page 65, lines 7 to 10,
- 21. Color coupler summary: page 65 lines 11 to 13.
- 5 22. Yellow, magenta and cyan couplers: page 65 lines 14 to 25,
 - 23. Polymer couplers: page 65 lines 26 to 28,
 - 24. Diffusive dye forming couplers: page 65 lines 29 to 31,
- 25. Colored couplers: page 65 lines 32 to 38,

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- 26. Functional coupler summary: page 65 lines 39 to 44,
- 27. Bleaching accelerator-releasing couplers: page 65 lines 45 to 48,
- 28. Development accelerator-releasing couplers: page 65 lines 49 to 53,
- 29. Other DIR couplers: page 65 line 54 to page 66 to line 4,
- 30. Method of dispersing couplers: page 66 lines 5 to 28,
- 31. Antiseptic and mildewproofing agents: page 66 lines 29 to 33,
 - 32. Types of sensitive materials: page 66 lines 34 to 36,
 - 33. Thickness of lightsensitive layer and swell speed:
 page 66 line 40 to page 67 line 1,
 - 34. Back layers: page 67 lines 3 to 8,
 - 35. Development processing summary: page 67 lines 9

to 11,

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- 36. Developing solution and developing agents: page 67 lines 12 to 30,
- 37. Developing solution additives: page 67 lines 31 to 44,
- 38. Reversal processing: page 67 lines 45 to 56,
- 39. Processing solution open ratio: page 67 line 57 to page 68 line 12,
- 40. Development time: page 68 lines 13 to 15,
- 10 41. Bleach-fix, bleaching and fixing: page 68 line 16 to page 69 line 31,
 - 42. Automatic processor: page 69 lines 32 to 40,
 - 43. Washing, rinse and stabilization: page 69 line 41 to page 70 line 18,
- 15 44. Processing solution replenishment and recycling: page 70 lines 19 to 23,
 - 45. Developing agent built-in sensitive material: page 70 lines 24 to 33,
 - 46. Development processing temperature: page 70 lines 34 to 38, and
 - 47. Application to film with lens: page 70 lines 39 to 41.

[0145]

Moreover, preferred use can be made of a bleaching solution containing 2-pyridinecarboxylic acid or 2,6-pyridinedicarboxylic acid, a ferric salt such as ferric nitrate and a persulfate as described in

EP No. 602,600. When this bleaching solution is used, it is preferred that the steps of stop and water washing be conducted between the steps of color development and bleaching. An organic acid such as acetic acid, succinic acid or maleic acid is preferably used as a stop solution. For pH adjustment and bleaching fog, it is preferred that the bleaching solution contains an organic acid such as acetic acid, succinic acid, maleic acid, glutaric acid or adipic acid in an amount of 0.1 to 2 mol/liter (hereinafter liter referred to as "L").

[0146]

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A magnetic recording layer usable in the present invention will be described below.

This magnetic recording layer is formed by coating the surface of a support with an aqueous or organic solvent-based coating solution which is prepared by dispersing magnetic grains in a binder.

[0147]

As the magnetic grains, it is possible to use grains of, e.g., ferromagnetic iron oxide such as γFe₂O₃, Co-deposited γFe₂O₃, Co-deposited magnetite, Co-containing magnetite, ferromagnetic chromium dioxide, a ferromagnetic metal, ferromagnetic alloy, Ba ferrite of a hexagonal system, Sr ferrite, Pb ferrite, and Ca ferrite. Co-deposited ferromagnetic iron oxide such as Co-deposited γFe₂O₃ is preferable. The grain can take

the shape of any of, e.g., a needle, rice grain, sphere, cube, and plate. The specific area is preferably 20 m 2 /g or more, and more preferably 30 m 2 /g or more as S_{BET}.

5 [0148]

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The saturation magnetization (σ s) of the ferromagnetic substance is preferably 3.0×10^4 to 3.0×10^5 A/m, and especially preferably 4.0×10^4 to 2.5×10^5 A/m. A surface treatment can be performed for the ferromagnetic grains by using silica and/or alumina or an organic material. Also, the surface of the ferromagnetic grain can be treated with a silane coupling agent or a titanium coupling agent as described in JP-A-6-161032. A ferromagnetic grain whose surface is coated with an inorganic or organic substance described in JP-A-4-259911 or JP-A-5-81652 can also be used.

[0149]

As a binder used together with the magnetic grains,

it is possible to use a thermoplastic resin described
in JP-A-4-219569, thermosetting resin, radiation-curing
resin, reactive resin, acidic, alkaline, or
biodegradable polymer, natural polymer (e.g., a
cellulose derivative and sugar derivative), and their

mixtures. The Tg of the resin is -40°C to 300°C, and
its weight average molecular weight is 2,000 to
1,000,000. Examples are a vinyl-based copolymer,

cellulose derivatives such as cellulosediacetate, cellulosetriacetate, celluloseacetatepropionate, celluloseacetatebutylate, and cellulosetripropionate, acrylic resin, and polyvinylacetal resin. Gelatin is 5 also preferable. Cellulosedi(tri)acetate is particularly preferable. This binder can be hardened by the addition of an epoxy-, aziridine-, or isocyanate-based crosslinking agent. Examples of the isocyanate-based crosslinking agent are 10 isocyanates such as tolylenediisocyanate, 4,4'-diphenylmethanediisocyanate, hexamethylenediisocyanate, and xylylenediisocyanate, reaction products of these isocyanates and polyalcohol (e.g., a reaction product of 3 mols of 15 tolylenediisocyanate and 1 mol of trimethylolpropane), and polyisocyanate produced by condensation of any of these isocyanates. These examples are described in JP-A-6-59357.

[0150]

As a method of dispersing the magnetic substance in the binder, as described in JP-A-6-35092, a kneader, pin type mill, and annular mill are preferably used singly or together. Dispersants described in JP-A-5-088283 and other known dispersants can be used. The thickness of the magnetic recording layer is 0.1 to 10 μ m, preferably 0.2 to 5 μ m, and more preferably 0.3 to 3 μ m. The weight ratio of the magnetic grains

to the binder is preferably 0.5:100 to 60:100, and more preferably 1:100 to 30:100. The coating amount of the magnetic grains is 0.005 to 3 g/m^2 , preferably 0.01 to 2 g/m^2 , and more preferably 0.02 to 0.5 g/m^2 . The transmitting yellow density of the magnetic recording layer is preferably 0.01 to 0.50, more preferably 0.03 to 0.20, and especially preferably 0.04 to 0.15.

[0151]

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The magnetic recording layer can be formed in the whole area of, or into the shape of stripes on, the back surface of a photographic support by coating or printing. As a method of coating the magnetic recording layer, it is possible to use any of an air doctor, blade, air knife, squeegee, impregnation, reverse roll, transfer roll, gravure, kiss, cast, spray, dip, bar, and extrusion. A coating solution described in JP-A-5-341436 is preferable.

[0152]

The magnetic recording layer can be given
a lubricating property improving function, curling
adjusting function, antistatic function, adhesion
preventing function, and head polishing function.
Alternatively, another functional layer can be
formed and these functions can be given to that layer.
A polishing agent in which at least one type of grains
are aspherical inorganic grains having a Mohs hardness

of 5 or more is preferable. The composition of this aspherical inorganic grain is preferably an oxide such as aluminum oxide, chromium oxide, silicon dioxide, titanium dioxide, and silicon carbide, a carbide such 5 as silicon carbide and titanium carbide, or a fine powder of diamond. The surfaces of the grains constituting these polishing agents can be treated with a silane coupling agent or titanium coupling agent. These grains can be added to the magnetic recording 10 layer or overcoated (as, e.g., a protective layer or lubricant layer) on the magnetic recording layer. A binder used together with the grains can be any of those described above and is preferably the same binder as in the magnetic recording layer. Sensitive 15 materials having the magnetic recording layer are described in US5, 336, 589, US5, 250, 404, US5, 229, 259, US5,215,874, and EP466,130.

[0153]

A polyester support used in the present invention

will be described below. Details of the polyester
support and sensitive materials, processing, cartridges,
and examples (to be described later) are described in
Journal of Technical Disclosure No. 94-6023 (JIII; 1994,
March 15). Polyester used in the present invention is
formed by using diol and aromatic dicarboxylic acid as
essential components. Examples of the aromatic
dicarboxylic acid are 2,6-, 1,5-, 1,4-, and

2,7-naphthalenedicarboxylic acids, terephthalic acid, isophthalic acid, and phthalic acid. Examples of the diol are diethyleneglycol, triethyleneglycol, cyclohexanedimethanol, bisphenol A, and bisphenol.

Examples of the polymer are homopolymers such as polyethyleneterephthalate, polyethylenenaphthalate, and polycyclohexanedimethanolterephthalate.

Polyester containing 50 to 100 mol% of 2,6-naphthalenedicarboxylic acid is particularly preferable. Polyethylene-2,6-naphthalate is especially preferable among other polymers.

[0154]

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The average molecular weight ranges between about 5,000 and 200,000. The Tg of the polyester of the present invention is 50° C or higher, preferably 90° C or higher.

[0155]

curling, the polyester support a resistance to curling, the polyester support is heat-treated at a temperature of 40°C to less than Tg, more preferably Tg - 20°C to less than Tg. The heat treatment can be performed at a fixed temperature within this range or can be performed together with cooling. The heat treatment time is 0.1 to 1500 hrs, more preferably 0.5 to 200 hrs. The heat treatment can be performed for a roll-like support or while a support is conveyed in the form of a web. The surface shape can also be

improved by roughening the surface (e.g., coating the surface with conductive inorganic fine grains such as SnO2 or Sb2O5). It is desirable to knurl and slightly raise the end portion, thereby preventing the cut portion of the core from being photographed. These heat treatments can be performed in any stage after support film formation, after surface treatment, after back layer coating (e.g., an antistatic agent or lubricating agent), and after undercoating.

A preferable timing is after the antistatic agent

[0156]

is coated.

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An ultraviolet absorbent can be incorporated into this polyester. Also, to prevent light piping, dyes or pigments such as Diaresin manufactured by Mitsubishi Kasei Corp. or Kayaset manufactured by NIPPON KAYAKU CO. LTD. commercially available for polyester can be incorporated.

[0157]

In the present invention, it is preferable to perform a surface treatment in order to adhere the support and the sensitive material constituting layers. Examples of the surface treatment are surface activation treatments such as a chemical treatment, mechanical treatment, corona discharge treatment, flame treatment, ultraviolet treatment, high-frequency treatment, glow discharge treatment, active plasma

treatment, laser treatment, mixed acid treatment, and ozone oxidation treatment. Among other surface treatments, the ultraviolet radiation treatment, flame treatment, corona treatment, and glow treatment are preferable.

[0158]

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An undercoating layer can include a single layer or two or more layers. Examples of an undercoating layer binder are copolymers formed by using, as 10 a starting material, a monomer selected from vinylchloride, vinylidenechloride, butadiene, methacrylic acid, acrylic acid, itaconic acid, and maleic anhydride. Other examples are polyethyleneimine, an epoxy resin, grafted gelatin, 15 nitrocellulose, and gelatin. Resorcin and p-chlorophenol are examples of a compound which swells a support. Examples of a gelatin hardener added to the undercoating layer are chromium salt (e.g., chromium alum), aldehydes (e.g., formaldehyde and 20 glutaraldehyde), isocyanates, an active halogen compound (e.g., 2,4-dichloro-6-hydroxy-s-triazine), epichlorohydrin resin, and active vinylsulfone compound. SiO₂, TiO₂, inorganic fine grains, or polymethylmethacrylate copolymer fine grains (0.01 to 25 10 μ m) can also be contained as a matting agent.

[0159]

In the present invention, an antistatic agent

is preferably used. Examples of this antistatic agent are carboxylic acid, carboxylate, a macromolecule containing sulfonate, cationic macromolecule, and ionic surfactant compound.

5 [0160]

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As the antistatic agent, it is especially preferable to use fine grains of at least one crystalline metal oxide selected from ZnO, TiO₂, SnO₂, Al₂O₃, In₂O₃, SiO₂, MgO, BaO, MoO₃, and V₂O₅, and having a volume resistivity of $10^7~\Omega \cdot \text{cm}$ or less, more preferably $10^5~\Omega \cdot \text{cm}$ or less and a grain size of 0.001 to 1.0 μ m, fine grains of composite oxides (e.g., Sb, P, B, In, S, Si, and C) of these metal oxides, fine grains of sol metal oxides, or fine grains of composite oxides of these sol metal oxides.

[0161]

The content in a sensitive material is preferably 5 to 500 mg/m², and especially preferably 10 to 350 mg/m^2 . The ratio of a conductive crystalline oxide or its composite oxide to the binder is preferably 1/300 to 100/1, and more preferably 1/100 to 100/5.

[0162]

A sensitive material of the present invention preferably has a slip property. Slip agent-containing layers are preferably formed on the surfaces of both a sensitive layer and back layer. A preferable slip property is 0.01 to 0.25 as a coefficient of kinetic

friction. This represents a value obtained when a stainless steel sphere 5 mm in diameter is conveyed at a speed of 60 cm/min (25%, 60%RH). In this evaluation, a value of nearly the same level is obtained when the surface of a sensitive layer is used as a sample to be measured.

[0163]

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Examples of a slip agent usable in the present invention are polyorganocyloxane, higher fatty acid amide, higher fatty acid metal salt, and ester of higher fatty acid and higher alcohol. As the polyorganocyloxane, it is possible to use, e.g., polydimethylcyloxane, polydiethylcyloxane, polydiethylcyloxane, polystyrylmethylcyloxane, or polymethylphenylcyloxane. A layer to which the slip agent is added is preferably the outermost emulsion layer or back layer.

Polydimethylcyloxane or ester having a long-chain alkyl group is particularly preferable.

[0164]

A sensitive material of the present invention preferably contains a matting agent. This matting agent can be added to either the emulsion surface or back surface and is especially preferably added to the outermost emulsion layer. The matting agent can be either soluble or insoluble in processing solutions, and the use of both types of matting agents is preferable. Preferable

examples are polymethylmethacrylate grains, poly(methylmethacrylate/methacrylic acid = 9/1 or 5/5 (molar ratio)) grains, and polystyrene grains. The grain size is preferably 0.8 to 10 μ m, and a narrow grain size distribution is preferable. It is preferable that 90% or more of all grains have grain sizes 0.9 to 1.1 times the average grain size. To increase the matting property, it is preferable to simultaneously add fine grains with a grain size of 0.8 μ m or smaller. Examples are polymethylmethacrylate grains (0.2 μ m), poly(methylmethacrylate/methacrylic acid = 9/1 (molar ratio, 0.3 μ m) grains, polystyrene grains (0.25 μ m), and colloidal silica grains (0.03 μ m).

15 [0165]

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A film cartridge used in the present invention will be described below. The principal material of the cartridge used in the present invention can be a metal or synthetic plastic.

20 Preferable plastic materials are polystyrene,
polyethylene, polypropylene, and polyphenylether.
The cartridge of the present invention can also contain
various antistatic agents. For this purpose, carbon
black, metal oxide grains, nonion-, anion-, cation-,
and betaine-based surfactants, or a polymer can be
preferably used. These cartridges subjected to the
antistatic treatment are described in JP-A-1-312537

and JP-A-1-312538. It is particularly preferable that the resistance be $10^{12}~\Omega$ or less at 25°C and 25%RH. Commonly, plastic cartridges are manufactured by using plastic into which carbon black or a pigment is incorporated in order to give a light-shielding property. The cartridge size can be a presently available 135 size. To miniaturize cameras, it is effective to decrease the diameter of a 25-mm cartridge of 135 size to 22 mm or less. The volume of a cartridge case is 30 cm³ or less, preferably 25 cm³ or less. The weight of plastic used in the cartridge and the cartridge case is preferably 5 to 15g.

[0166]

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rotating a spool can be used in the present invention.

It is also possible to use a structure in which a film leader is housed in a cartridge main body and fed through a port of the cartridge to the outside by rotating a spool shaft in the film feed direction.

These structures are disclosed in USP Nos. 4,834,306 and 5,226,613. Photographic films used in the present invention can be so-called raw films before being developed or developed photographic films. Also, raw and developed photographic films can be accommodated in the same new cartridge or in different cartridges.

[0167]

A color photographic lightsensitive material of

the present invention is also suitably used as a negative film for an advanced photo system (to be referred to as an APS hereinafter). Examples are NEXIA A, NEXIA F, and NEXIA H (ISO 200, 100, and 400,

respectively) manufactured by Fuji Photo Film Co., Ltd. (to be referred to as Fuji Film hereinafter). These films are so processed as to have an APS format and set in an exclusive cartridge. These APS cartridge films are loaded into APS cameras such as the Fuji Film EPION Series represented by the EPION 300Z. A color light sensitive film of the present invention is also suited as a film-fitted lens such as Fuji Film FUJICOLOR UTSURUNDESU (Quick Snap) SUPER SLIM.

[0168]

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- A photographed film is printed through the following steps in a miniature laboratory system.
 - (1) Reception (an exposed cartridge film is received from a customer)
 - (2) Detaching step (the film is transferred from the cartridge to an intermediate cartridge for development)
 - (3) Film development
 - (4) Reattaching step (the developed negative film is returned to the original cartridge)
- (5) Printing (prints of three types C, H, and P and an index print are continuously automatically printed on color paper [preferably Fuji Film SUPER FA8])
 - (6) Collation and shipment (the cartridge and the

index print are collated by an ID number and shipped
together with the prints)

[0169]

As these systems, the Fuji Film MINILABO CHAMPION SUPER FA-298, FA-278, FA-258, FA-238 and Fuji Film DIGITALLABO SYSTEM, FRONTIER are preferable. Examples of a film processor for the MINILABO CHAMPION are the FP922AL/FP562B/FP562B, AL/FP362B/FP362BL AL and a recommended processing chemical is the FUJICOLOR JUST-IT CN-16L and CN-16Q. Examples of a printer processor are the PP3008AR/PP3008A/PP1828AR/PP1828A/PP1258AR/PP1258A/PP728AR/PP728A, and a recommended processing chemical is the FUJICOLOR JUST-IT CP-47L and CP-40FAII.

15 [0170]

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In the FRONTIER SYSTEM, SCANNER & IMAGE-PROCESSOR SP-1000 and LASER PRINTER & PAPER PROCESSOR LP-1000P, or LASER PRINTER LP-1000W are used. A detacher used in the detaching step and a reattacher used in the reattaching step are preferably the Fuji Film DT200 or DT100 and AT200 or AT100, respectively.

[0171]

The APS can also be enjoyed by PHOTO JOY SYSTEM whose main component is the Fuji Film Aladdin 1000 digital image scanner. For example, a developed APS cartridge film is directly loaded into the Aladdin 1000, or image information of a negative film, positive film,

or print is input to the Aladdin 1000 by using the FE-550 35-mm film scanner or the PE-550 flat head scanner. Obtained digital image data can be easily processed and edited. This data can be printed out by the NC-550AL digital color printer using a photo-fixing heat-sensitive color printing system or the PICTOROGRAPHY 3000 using a laser exposure thermal development transfer system, or by existing laboratory equipment through a film recorder. The Aladdin 1000 can also output digital information directly to a floppy disk or Zip disk or to an CD-R via a CD writer.

[0172]

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In a home, a user can enjoy photographs on a TV set simply by loading a developed APS cartridge film 15 into the Fuji Film Photo Player AP+1. Image information can also be continuously input to a personal computer by loading a developed APS cartridge film into the Fuji Film Photo Scanner AS-1. The Fuji Film Photo Vision FV-10 or FV-5 can be used to input a film, print, 20 or three-dimensional object. Furthermore, image information recorded in a floppy disk, Zip disk, CD-R, or hard disk can be variously processed on a computer by using the Fuji Film Photo Factory application software. The Fuji Film NC-2 or NC-2D digital color 25 printer using a photo-fixing heat-sensitive color printing system is suited to outputting high-quality prints from a personal computer.

[0173]

To keep developed APS cartridge films, the FUJICOLOR POCKET ALBUM AP-5 POP L, AP-1 POP L, or AP-1 POP KG, or the CARTRIDGE FILE 16 is preferable.

5 [0174]

[EXAMPLE]

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The present invention will be described in greater detail below by way of its examples. However, the present invention is in no way limited to these examples.

[0175]

(Example 1)

A color lightsensitive material to be charged in a lens-fitted lightsensitive material packaging unit was produced in the following manner.

Silver halide emulsions were produced in the following manner.

[0176]

Preparation of emulsion Em-K

20 (Preparation of seed emulsion)

1200 mL of an aqueous solution containing 1.0 g of a low-molecular-weight oxidized gelatin whose weight average molecular weight was 15,000 and 0.9 g of KBr was vigorously agitated while maintaining the temperature thereof at 35°C. 40 mL of an aqueous solution containing 1.85 g of AgNO3 and 35 mL of an aqueous solution containing 1.82 g of KBr and 1.0 g of

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a low-molecular-weight gelatin whose weight average molecular weight was 15,000 were added by the double jet method over a period of 30 sec to thereby effect a nucleation. Immediately after the completion of addition, 5.4 g of KBr was added and heated to 75° C, and the mixture was ripened. After the completion of ripening, 35 g of gelatin obtained by chemically modifying an alkali-processed gelatin of 100 thousand weight average molecular weight with succinic anhydride was added. Thereafter, the pH was adjusted to 5.5. 250 mL of an aqueous solution containing 36 g of AgNO3 and 282 mL of an aqueous solution containing 21.2 g of KBr and 2.81 g of KI were added by the double jet method over a period of 25 min, while maintaining the silver potential at -5 mV. Thereafter, 650 mL of an aqueous solution containing 200 g of $AgNO_3$ and 900 mL of an aqueous solution containing 134.1 g of KBr and 13.9 g of KI were added by the double jet method over a period of 100 min while increasing the flow rate so that the final flow rate was 1.4 times the initial flow rate. During this period, the silver potential was maintained at +5 mV against saturated calomel electrode. The thus obtained emulsion was washed, and gelatin was added so that the pH was adjusted to 5.7, the pAg to 8.8, the weight in terms of silver per kg of emulsion to 139.0 g and the gelatin weight to 56 g. Thus, a seed emulsion was obtained.

[0177]

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1200 mL of an aqueous solution containing 33 g of g of lime-processed gelatin having a calcium concentration of 1 ppm and 3.4 g of KBr was vigorously agitated while maintaining the temperature thereof at 75° C. 89 g of the above seed emulsion was added, and further 0.3 of modified silicone oil (L7602, produced by Nippon Unicar Company, Limited) was added. ${\rm H}_2{\rm SO}_4$ was added to thereby adjust the pH value to 5.8. 2 mg of sodium benzenethiosulfonate and 2 mg of thiourea dioxide were added. 600 mL of an aqueous solution containing 51.0 g of AgNO $_3$ and 600 mL of an aqueous solution containing 36.2 g of KBr and 3.49 g of KI were added by the double jet method over a period of 85 min while increasing the flow rate so that the final flow rate was 1.1 times the initial flow rate. During this period, the silver potential was maintained at $-35~\mathrm{mV}$ against saturated calomel electrode. Further, 300 mL of an aqueous solution containing $44.7\ \mathrm{g}$ of $\mathrm{AgNO_3}$ and 300 mL of an aqueous solution containing 30.6 g of KBr and 3.06 g of KI were added by the double jet method over a period of 56 min while increasing the flow rate so that the final flow rate was 1.1 times the initial flow rate. During this period, the silver potential was maintained at $-35~\mathrm{mV}$ against saturated calomel electrode.

Subsequently, an aqueous solution of KBr and 180 mL of an aqueous solution containing 36.9 g of $AgNO_3$ were added over a period of 40 min. During this period, the silver potential was maintained at +10 mV against saturated calomel electrode. KBr was added so as to adjust the silver potential to -70 mV. Thereafter, 1.38 g, in terms of the weight of KI, of AgI fine grain emulsion of $0.037 \mu m$ grain size was added. Immediately after the completion of addition, 100 mL of an aqueous solution containing 17.4 g of AgNO3 was added over a period of 15 min. The mixture was washed with water, and gelatin was added so as to adjust the pH and pAg at 40°C to 5.8 and 8.7, respectively. This emulsion was heated to 60°C , and compound 2 and sensitizing dyes ExS-10 and ExS-13 were added. The optimum chemical sensitization thereof was effected by the addition of potassium thiocyanate, chloroauric acid, sodium thiosulfate, hexafluorophenyldiphenylphosphine selenide, compound (F-11) and compound 3. At the completion of chemical sensitization, compound (F-3) defined later was added.

[0179]

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The thus obtained emulsion contained tabular grains having an average equivalent sphere diameter of $1.65~\mu m$, an average equivalent circle diameter of $3.10~\mu m$, a variation coefficient of equivalent circle diameter of 20% and an average aspect ratio of 10.0.

The ratio in projected area of grains having an aspect ratio of 5 or more to all the grains was 90%. The twin plane spacing, measured in the aforementioned manner, was 0.015 μm .

5 [0180]

The thus obtained grains were observed through a transmission electron microscope while cooling the same with liquid nitrogen. As a result, it was found that grains each having no dislocation line in a region extending from the grain center to 80% of its projected area constituted about 98% of all the grains, and that there were 10 or more dislocation lines per grain on grain peripheral portions extending from the grain extreme periphery to 20% of the projected area.

15 [0181]

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Preparation of emulsions Em-A/E

1300 mL of an aqueous solution containing 1.6 g of a low-molecular-weight oxidized gelatin whose weight average molecular weight was 15,000 and 1.0 g of KBr was vigorously agitated while maintaining the temperature at 58° C and adjusting the pH to 9.

[0182]

An aqueous solution containing 1.3 g of AgNO₃ and an aqueous solution containing 1.1 g of KBr and 0.7 g of a low-molecular-weight gelatin whose weight average molecular weight was 15,000 were added by the double jet method over a period of 30 sec to thereby effect a

nucleation. 6.6 g of KBr was added and heated to 78° C, and the mixture was ripened. After the completion of ripening, 15.0 g of gelatin obtained by chemically modifying an alkali-processed gelatin of 100 thousand weight average molecular weight with succinic anhydride was added. Thereafter, the pH was adjusted to 5.5. aqueous solution containing 15.8 g of KBr and 1.92 g of KI and 230 mL of an aqueous solution containing 29.3 g of AgNO3 were added by the double jet method over a period of 30 min. During this period, the silver potential was maintained at -20 mV against saturated calomel electrode. Thereafter, an aqueous solution containing 64.5 g of AgNO3 and 233 mL of an aqueous solution containing 42.3 g of KBr and 5.14 g of KI were added by the double jet method over a period of 37 min while increasing the flow rate so that the final flow rate was 1.33 times the initial flow rate. During this period, while the addition was being effected, the silver potential was maintained at -20 mV. Thereafter, an aqueous solution containing 70.8 g of AgNO3 and an aqueous solution of KBr were added by the double jet method over a period of 35 min, while maintaining the silver potential at -10 mV.

[0183]

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The mixture was cooled to 40°C , and 4.9~g of compound 1 was added. Further, 32 mL of a 0.8 M aqueous sodium sulfite solution was added. The mixture

had its pH value adjusted to 9.0 with the use of an aqueous solution of NaOH and was held still for 5 min. The resultant mixture was heated to 55° C, and the pH value thereof was adjusted to 5.5 with H₂SO₄. sodium benzenethiosulfonate was added, and further 13 g of lime-processed gelatin having a calcium concentration of 1 ppm was added. After the completion of addition, an aqueous solution of KBr and 250 mL of an aqueous solution containing 71.0 g of AgNO3 were added over a period of 20 min, while maintaining the silver potential at +75 mV. During this period, 1.0×10^{-5} mol of yellow prussiate of potash was added per mol of silver, and 1 \times 10⁻⁸ mol of K₂IrCl₆ added per mol of silver. The mixture was washed with water, and gelatin was added so as to adjust the pH and pAq at 40° C to 6.5 and 8.8, respectively.

[0184]

The thus obtained emulsion contained tabular grains having an average equivalent sphere diameter of 1.33 μ m, an average equivalent circle diameter of 2.63 μ m and an average aspect ratio of 11.4. The ratio in projected area of grains having an aspect ratio of 5 or more to all the grains was 95%, and the twin plane spacing of tabular grains was 0.012 μ m.

25 [0185]

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The thus obtained grains were observed through a transmission electron microscope while cooling the same

with liquid nitrogen. As a result, it was found that grains each having no dislocation line in a region extending from the grain center to 80% of its projected area constituted about 90% of all the grains, and that there were 10 or more dislocation lines per grain on grain peripheral portions extending from the grain extreme periphery to 20% of the projected area.

[0186]

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(Preparation of emulsion Em-A)

The obtained emulsion was heated to 56℃, and compound 2 and sensitizing dyes ExS-1, ExS-2 and ExS-3 were added. Thereafter, the optimum chemical sensitization thereof was effected by the addition of potassium thiocyanate, chloroauric acid, sodium thiosulfate, hexafluorophenyldiphenylphosphine selenide, compound (F-11) defined later and compound 3. At the completion of chemical sensitization, compound (F-2) defined later was added.

[0187]

(Preparation of emulsion Em-E)

Emulsion Em-E was prepared in the same manner as the emulsion Em-B, except that the chemical sensitization was carried out with the sensitizing dyes changed to sensitizing dyes ExS-7, ExS-8 and ExS-9.

25 [0188]

(Preparation of emulsion Em-N)

1250 mL of an aqueous solution containing 48 g of

deionized gelatin and 0.75 g of KBr was vigorously agitated while maintaining the temperature at 70° C.

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276 mL of an aqueous solution containing 12.0 g of AgNO3) and an equimolar-concentration aqueous solution of KBr were added to the aqueous solution by the double jet method over a period of 7 min while maintaining the pAg at 7.26. Subsequently, 600 mL of an aqueous solution containing 108.0 g of AgNO3 and an equimolarconcentration aqueous solution of a mixture of KBr and KI (2.0 mol% KI) were added by the double jet method over a period of 18 min 30 sec while maintaining the pAg at 7.30. Further, 18.0 mL of a 0.1% by weight aqueous thiosulfonic acid solution was added 5 min before the completion of the addition. The obtained emulsion was desalted and washed by the customary flocculation method, and re-dispersed. At 40° C, the pH and pAg were adjusted to 6.2 and 7.6, respectively. The temperature of the emulsion was controlled at 40° C, and compound 2 and sensitizing dyes ExS-10 and ExS-12 were added. Further, potassium thiocyanate, chloroauric acid, sodium thiosulfate, hexafluorophenyldiphenylphosphine selenide, compound (F-11) and compound 3 were added to the emulsion, and heated to 68° C to thereby effect the optimum chemical sensitization thereof. At the completion of chemical sensitization, compound (F-2) defined later was added.

The obtained emulsion contained cubic grains

having an equivalent sphere diameter of 0.19 μm and a variation coefficient of equivalent sphere diameter of 14%.

[0189]

5 Emulsions Em-B to D, Em-F to J, and Em-L to R were prepared in the same manner as the above emulsions Em-A, E and K, except that the temperature, pH, silver potential, amount of silver nitrate, amount of KI, amount of compounds, type of sensitizing dyes, amount of seed emulsion, etc. were appropriately changed.

Lists of the thus obtained emulsions are given in Table 1.

[0190] [Table 1]

Table 1

	Equivalent		Equivalent			
	circle diameter	Aspect ratio	sphere diameter	Grain shape	<pre>Dislocation line (number/grain)</pre>	spacing
	(m m)		(# m)			(m n/)
Em-A	2.63	11.4	1.33	Tabular	10 or more	0.012
Em-B	1.50	6.0	0.80	Tabular	10 or more	0.012
Em-C	0.85	7.1	0.51	Tabular	10 or more	0.012
Em-D	0.40	2.7	0.35	Tabular	10 or more	0.011
Em-E	2.63	11.4	1.33	Tabular	10 or more	0.012
Em-F	2.00	3.0	0.92	Tabular	10 or more	0.013
Em-G	1.60	7.0	0.79	Tabular	10 or more	0.012
Em-H	0.85	7.1	0.51	Tabular	10 or more	0.012
Em-I	0.58	3.2	0.45	Tabular	10 or more	0.010
Em-J	2.00	7.0	0.92	Tabular	10 or more	0.012
Em-K	3.10	10.0	1.65	Tabular	10 or more	0.015
Em-L	1.25	4.3	0.89	Tabular	10 or more	0.011
Em-M	0.55	4.6	0.37	Tabular	10 or more	0.010
Em-N	1	•	0.19	Cubic	•	-
Em-O	1.76	9.5	0.95	Tabular	10 or more	0.012
Em-P	2.20	6.9	1.33	Tabular	10 or more	0.013
Em-Q	1.50	0.9	0.80	Tabular	10 or more	0.012
Em-R	0.85	7.1	0.51	Tabular	10 or more	0.012

[0191]

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Preparation of coating sample

A support of cellulose triacetate film furnished with a substratum was coated with a plurality of layers of the following compositions, thereby preparing multilayer color lightsensitive material sample 101.

(Composition of lightsensitive layer)

Main materials for use in each layer are classified as follows:

10 ExC: cyan coupler; ExS: spectral sensitizing dye

UV: ultraviolet absorber;

ExY: yellow coupler; H: gelatin hardener

(For each specific compound, in the following description, numeral is assigned after the character, and the formula is shown later).

[0192]

The figure given beside the description of each component is for the coating amount expressed in the unit of g/m^2 . With respect to a silver halide, the coating amount is in terms of silver. With respect to a spectral sensitizing dye, the coating amount is expressed in the unit of mol per mol of silver halide present in the same layer.

[0193]

1st layer (1st antihalation layer)

Black colloidal silver silver 0.070

	Gelatin		0.660
	ExM-1		0.048
	Cpd-2		0.001
•	F-8		0.001
5	HBS-1	• .	0.090
	HBS-2		0.010
	[0194]		
	2nd layer (2nd antiha	alation layer)	
	Black colloidal	silver silver	0.090
10	Gelatin		0.830
	ExM-1		0.057
	ExF-1		0.002
	F-8		0.001
	HBS-1		0.090
15	HBS-2		0.010
	[0195]		
	3rd layer (Interlayer	·)	
	ExC-2		0.010
	Cpd-1		0.086
20	UV-2		0.029
	UV-3		0.052
	UV-4		0.011
	HBS-1		0.100
	Gelatin		0.580
25	[0196]		
	4th layer (Low-speed	red-sensitive emu	lsion layer)
	Em-D	silver	0.47

	Em-	-C	silver	0.57	
	ExC	2-1		0.222	
	ExC	:-2		0.010	
	ExC	:-3		0.072	
5	ExC	<u>:</u> – 4		0.101	
	ExC	:-5		0.005	
	ExC	-6		0.008	
	ExC	-8		0.071	
	ExC	-9		0.010	
10	ExS	-1		1.4 ×	10-3
•	ExS	-2		6.0 ×	10-4
	ExS	-3		2.0 ×	10-5
	UV-	2		0.036	
	UV-	3		0.067	
15	UV-	4		0.014	
	Cpd-	-2		0.010	
	Cpd-	-4		0.012	
	HBS-	-1		0.240	
	HBS-	-5 .		0.010	
20	Gela	atin		1.630	
		[0197]			
	5th layer	(Medium-speed	red-sensitive	emulsion	layer)
	Em-E	3	silver	0.63	
	ExC-	-1		0.111	
25	ExC-	-2		0.039	
	ExC-	-3		0.018	
	ExC-	- 4		0.074	

		ExC-5	5		0.019
		ExC-6	6		0.024
		ExC-8	3		0.010
		ExC-9	e		0.005
5		ExS-1	L		6.3×10^{-4}
		ExS-2	2		2.6×10^{-4}
-		ExS-3	3		8.7×10^{-6}
		Cpd-2	2		0.020
		Cpd-4	1		0.021
10		HBS-1	L		0.129
		Gelat	in		0.900
			[0198]		
	6th	layer	(High-speed	red-sensitive emul	sion layer)
-		Em-A		silver	1.27
15		ExC-1	-		0.122
		ExC-6			0.032
		ExC-8	}		0.110
		ExC-9			0.005
		ExC-1	. 0		0.159
20		ExS-1			3.2×10^{-4}
		ExS-2)		2.6×10^{-4}
		ExS-3	}	1	8.8×10^{-6}
•		Cpd-2			0.068
		Cpd-4			0.015
25		HBS-1			0.440
		Gelat	in		1.610
			[0199]		

	7th layer (Interlayer) .
	Cpd-1	0.081
	Cpd-6	0.002
	Solid disperse d	ye ExF-4 0.015
5	HBS-1	0.049
	Polyethyl acryla	te latex 0.088
	Gelatin	0.759
	[0200]	
	8th layer (Layer capa	ole of exerting interlayer effect
10	on red-sensitive laye	r)
	Em-J	silver 0.40
	Cpd-4	0.010
	ExM-2	0.082
	ExM-3	0.006
15	E×M-4	0.026
	ExY-1	. 0.010
	ExY-4	0.040
	ExC-7	0.007
	ExS-4	7.0×10^{-4}
20	ExS-5	2.5×10^{-4}
	HBS-1	0.203
	HBS-3	0.003
	HBS-5	0.010
	Gelatin	0.570
25	[0201]	
	9th layer (Low-speed g	reen-sensitive emulsion layer)
	Em-H	silver 0.23

	Em-G	silver 0.15	
	Em-I	silver 0.26	
	ExM-2	0.388	
	ExM-3	0.040	
5	ExY-1	0.003	
	ExY-3	0.002	
	ExC-7	0.009	
	ExS-5	3.0 × 10 ⁻	4
	ExS-6	8.4 × 10 ⁻	5
10	ExS-7	1.1 × 10 ⁻	4
	ExS-8	4.5 × 10 ⁻	4
	ExS-9	1.3 × 10 ⁻	4
	HBS-1	0.337	
	HBS-3	0.018	
15	HBS-4	0.260	
	HBS-5	0.110	
	Cpd-5	0.010	•
	Gelatin	1.470	
	[0202]		
20	Oth layer (Medium-speed	d green-sensitive emulsion l	ayer)
	Em-F	silver 0.42	
	ExM-2	0.084	
	ExM-3	0.012	
	E×M-4	0.005	
25	ExY-3	0.002	
	ExC-6	0.003	
	ExC-7	0.007	

		ExC-8			0.008	
		ExS-7			1.0×10^{-4}	
		ExS-8			7.1×10^{-4}	
		ExS-9			2.0×10^{-4}	
5		HBS-1	,		0.096	
		HBS-3			0.002	
		HBS-5			0.002	
•		Cpd-5			0.004	
		Gelati	in		0.382	
10			[0203]			
	11th	layer	(High-speed	green-sensitive	emulsion laye	er)
		Em-Z		silver	0.95	
		ExC-6			0.002	
		ExC-8			0.010	
15		ExM-1			0.014	
		ExM-2			0.023	
		ExM-3			0.023	
		ExM-4			0.005	
		ExM-5			0.040	
20		ExY-3			0.003	
		ExS-7			8.4×10^{-4}	
		ExS-8			5.9×10^{-4}	
		ExS-9			1.7×10^{-4}	
		Cpd-3			0.004	
25		Cpd-4			0.007	
		Cpd-5			0.010	
		HBS-1			0.259	

		HBS-5		0.020
		Polyethyl acrylate	latex	0.099
		Gelatin		0.781
		[0204]		
5	12th	layer (Yellow filte	er layer)	
		Cpd-1		0.088
		Solid disperse dye	ExF-2	0.051
		Solid disperse dye	ExF-8	0.010
		HBS-1		0.049
10		Gelatin		0.593
		[0205]		
	13th	layer (Low-speed bl	ue-sensitive em	ulsion layer)
		Em-N	silver	0.12
		Em-M	silver	0.09
15		Em-L	silver	0.50
		ExC-1		0.024
		ExC-7		0.011
		ExY-1		0.002
		ExY-2		0.956
20		ExY-4		0.091
		ExS-10		8.5×10^{-5}
		ExS-11		6.4×10^{-4}
		ExS-12		8.5×10^{-5}
		ExS-13	·	5.0×10^{-4}
25		Cpd-2		0.037
		Cpd-3		0.004
		HBS-1		0.372

		HBS-5				0.047	
		Gelati	.n			2.201	
			[0206]				
	14th	layer	(High-speed	blue-se	nsitive	emulsion	layer)
5		Em-X			silver	1.22	
		ExY-2	,			0.235	
		ExY-4			٠	0.018	
•		ExS-10				1.5 ×	10-4
		ExS-13				2.0 ×	10-4
10		Cpd-2				0.075	
		Cpd-3				0.001	
		HBS-1				0.087	
		Gelati	n .			1.156	
		[0207]				
15	15th	layer	(1st protect:	ive laye	er)		
		0.07 μ	m silver iod	obromid	e emulsi	on	
					silver	0.28	
		UV-1				0.358	
•		UV-2				0.179	
20		UV-3			·	0.254	
		UV-4				0.025	
		F-11				0.0081	
		SA-1				0.078	
		ExF-5				0.0024	
25		ExF-6				0.0012	
		ExF-7				0.0010	
		HBS-1				0.175	

	HBS-4	0.050
	Gelatin	2.231
	[0208]	
	16th layer (2nd protective layer)	
5	H-1	0.400
	B-1 (diameter 1.7 μ m)	0.050
•	B-2 (diameter 1.7 μ m)	0.150
	B-3·	0.050
	SA-1	0.200
10	Gelatin	0.711.
	[0209]	
	In addition to the above comp	onents, W-1 to W-6,
	B-4 to B-6, F-1 to F-17, a lead sa	lt, a platinum salt,
	an iridium salt and a rhodium salt	were appropriately
15	added to the above individual laye	rs in order to
	improve the storage life, processal	bility, resistance to
	pressure, antiseptic and mildewpro	ofing properties,
	antistatic properties and applicab	ility thereof.
	[0210]	
20	Preparation of dispersion of	organic solid
	disperse dye:	
	The ExF-2 of the 12th layer w	as dispersed by the
	following method. Specifically,	
	Wet cake of ExF-2 (contg. 17.	6 wt.% water)
25		2.800 kg
	Sodium octylphenyldiethoxymeth	nanesulfonate

(31 wt.% aq. soln.)

0.376 kg

F-15 (7% aq. soln.)

 $0.011 \, kg$

Water

4.020 kg

Total

7.210 kg

(adjusted to pH = 7.2 with NaOH).

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[0211]

Slurry of the above composition was agitated by means of a dissolver to thereby effect a preliminary dispersion, and further dispersed by means of agitator mill LMK-4 under such conditions that the peripheral speed, delivery rate and packing ratio of 0.3 mm-diameter zirconia beads were 10 m/s, 0.6 kg/min and 80%, respectively, until the absorbance ratio of the dispersion became 0.29. Thus, a solid particulate dispersion was obtained, wherein the average particle diameter of dye particulate was 0.29 μ m.

[0212]

Solid dispersions of ExF-4 and ExF-8 were obtained in similar manners. The average particle diameters of these dye particulates were 0.28 μm and 0.49 μm , respectively.

The compounds employed in the emulsion preparation and compounds incorporated in the above layers in the preparation of coating sample will be specified below.

[Chem 9] ExS-1
$$O$$
 C_2H_5 C_1 C_2H_5 C_1 C_1 C_2H_5 C_2H_5 C_1 C_2H_5 C_2H_5 C_1 C_2H_5 C_2H_5 C_1 C_2H_5 C_2H_5 C_2H_5 C_1 C_2H_5 C_2H_5 C_2H_5 C_2H_5 C_2H_5 C_1 C_2H_5 C_2H_5

5 [0214] [Chem 10]

ExS-2
$$C_2H_5$$
 C_2H_5 C_2H_5 C_1 C_1 C_1 C_2H_2 C_3 C_4 C_5 C_5 C_6 C_7 C_8 C_8

10 [0215] [Chem 11]

ExS-3
$$C_2H_5$$
 C_2H_5 C_2H_5 C_2H_5 C_2H_5 C_2H_5 C_2H_5 C_2H_5 C_2H_5

[0216] [Chem 12]

Compound 1

10 Compound 2

5

15

20

[0219] [Chem 15]

Compound 3

[0220] [Chem 16]

Compound 5

[0221] [Chem 17]

ExS-5

ExS-6

ExS-7

ExS-8

$$\begin{array}{c|c} & C_2H_5 \\ & CH=C-CH \\ & N \\ & CH_2)_4SO_3 \\ & (CH_2)_4SO_3Na \\ \end{array}$$

10

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[0222] to [0225] [Chem 18] to [Chem 21]

ExS-10

$$CI \xrightarrow{S} CH \xrightarrow{O} O$$

$$SO_3$$

$$SO_3$$

$$SO_3$$

ExS-11

CI
$$CH_{2}$$
 CH_{3} CH_{2} CH_{2} CH_{3} CH_{2} CH_{3} CH_{2} CH_{3} CH_{2} CH_{3} CH_{2} CH_{3} CH_{2} CH_{3} CH_{3} CH_{2} CH_{3} CH_{3}

ExS-12

ExS-13

$$CI \xrightarrow{S} CH \xrightarrow{S} CI$$

$$SO_3^- SO_3^- \cdot (Et)_3NH$$

ExC-1

ExC-6

ExM-1

$$(t)C_5H_{11} - OCHCONH$$

$$C_5H_{11}(t) - CONH N=N-OCH_3$$

$$N N O$$

$$CI - CI$$

ExM-2

ExM-3

$$C_{2}H_{5}$$
 $C_{2}H_{5}$
 $C_{2}H_{5}$
 C_{1}
 $C_{2}H_{5}$
 $C_{2}H_{5}$
 C_{1}
 $C_{2}H_{5}$
 C_{1}
 $C_{2}H_{5}$
 C_{1}
 C_{1}
 $C_{2}H_{5}$
 $C_{1}H_{5}$
 $C_{1}H_{5}$
 $C_{2}H_{5}$
 $C_{2}H_{5}$
 $C_{3}H_{5}$
 $C_{4}H_{5}$
 $C_{5}H_{5}$
 $C_{5}H_{5}$

ExM-4

$$\begin{array}{c} \text{CH}_{3} \\ \text{N} \\ \text{N} \\ \text{N} \\ \text{N} \\ \text{N} \\ \text{O}(\text{CH}_{2})_{2}\text{OC}_{2}\text{H}_{5} \\ \\ \text{C}_{5}\text{H}_{11}(t) \\ \\ \text{CH}_{3} \\ \\ \text{NHCOCHO} \\ \\ \text{C}_{6}\text{H}_{13} \\ \end{array}$$

ExM-5

$$tC_5H_{11}$$
 C_2H_5
 C_5H_{11}
 C_2H_5
 C_5H_{11}
 C_2H_5
 C_5H_{11}
 C_2H_5
 C_5H_{11}
 C_2H_5
 C_5H_{11}
 C_2H_5
 C_1
 C_1
 C_1
 C_1

EXY-1 CH₃ CH₃ COOCHCOOC₁₂H₂₅

COOCHCOOC₁₂H₂₅

COOCHCOOC₁₂H₂₅

COOCHCOOC₁₂H₂₅(n)

EXY-2 COOCHCONH

O=C

$$C_2H_5O$$

CH₃

NHCO(CH₂)₃O

 $C_5H_{11}(t)$

EXY-4

CH₃

NHCO(CH₂)₃O

 $C_5H_{11}(t)$

CH₃

NHCO(CH₂)₃O

 $C_5H_{11}(t)$

CH₃

NHCO(CH₂)₃O

 $C_5H_{11}(t)$

[0231] [Chem 27]

B-1

B-2

B-3 (Molar ratio)

Av. Molecular wt.: about8,000

B-4

Av. Molecular wt.: about750,000

B-5 $-(CH_2-CH_y) \times (-CH_2-CH_y) \times (-CH_y) \times$

Av. molecular wt.: about10,000

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SA-1

$$O = \bigvee_{\substack{N \\ H}} \bigvee_{\substack{N \\ H}} O$$

HBS-1 Tricresyl phosphate

HBS-2 Di-n-butyl phthalate

HBS-3 (t)
$$C_5H_{11}$$
 — OCHCONH — CO₂H

HBS-4 Tri(2-ethylhexyl) phosphate

F-1

F-2

F-3

F-4

$$O_2N$$

F-5

F-6

F-7

$$C_2H_5$$
 $C_4H_9CHCONH$
 N
 N
 N

F-8

F-9

(CH₂)₄COOH

F-10

F-11

HONH N NHOH
N N
N
$$(C_2H_5)_2$$

F-12

F-13

$$CH_3$$
— SO_2Na

F-14

$$\bigcirc$$
 SO₂SNa

F-15

F-16

F-17

$$HO-\left\langle \bigcirc \right\rangle -COOC_4H_9$$

W-1 $C_8F_{17}SO_2NHCH_2CH_2CH_2CH_2CH_2CH_2CH_2N(CH_3)_3$ CH_3 — SO_3^{Θ}

W-2
$$C_8H_{17}$$
 OCH_2CH_2 OCH_2CH_2 OCH_2CH_3 OCH_2 OCH_2

W-3 $iso-H_7C_3 \qquad C_3H_7-iso$ C_3H_7-iso $SO_3H \qquad Na$

W-5 C_2H_5 $(n)C_4H_9CHCH_2COOCH_2$ $(n)C_4H_9CHCH_2COOCHSO_3Na$ C_2H_5

W-6
$$\begin{array}{c} \text{CH}_{3} \\ \text{H} \\ \text{C}_{8}\text{F}_{17}\text{SO}_{2}\text{NCH}_{2}\text{CH}_{2}\text{N} \xrightarrow{-} \text{CH}_{3} \cdot \text{I} \\ \text{CH}_{3} \end{array}$$

ExC-7 OH CONH OCH₃
$$C_{12}H_{25}$$
 C N $C_{12}C_{12}$

ExC-9

ExC-10 OH
$$CONH(CH_2)_3O-nC_4H_9$$
 $i-C_4H_9-O-CNH$ $OCH_2CH_2SCHCOOH$ $OCH_2CH_2SCHCOOH$ $OCH_2CH_2SCHCOOH$

ExF-1

CI CH₃ CH₃ CH₃ CH₃ CH

CH-CH=CH

$$\begin{array}{c} CH_3 \\ CI \\ C_2H_5 \end{array}$$
 $\begin{array}{c} CH_3 \\ C_2H_5 \end{array}$
 $\begin{array}{c} CH_3 \\ C_2H_5 \end{array}$

ExF-2

ExF-4

5

ExF-7

HOOC
$$N-NH$$

SO₃H

ExF-8
$$NH-SO_2-C_4H_9$$

$$CN$$

$$CH$$

Samples 102 to 107 having each ISO speed were prepared in the same manner as the above sample 101, except that in the emulsion layers, silver halide emulsions Em-A to P were used with the silver amounts set forth in Table 2.

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101	1600	D 0.47	C 0.57	В 0.63	A 1.27		J 0.40	Н 0.23	G 0.15	I 0.26	F 0.42		E 0.95		N 0.12	0.09 M	L 0.50	К 1.22	
107	800	D 0.50	C 0.42	В 0.93	0 1.29		0 0.31	н 0.22	G 0.45	I 0.31	G 0.40		F 0.87		N 0.13	M 0.12	L 0.39	P 0.91	
106	640	D 0.46	C 0.39	В 0.90	0 1.25		0.30	н 0.20	G 0.30	I 0.45	G 0.41		F 0.85		N 0.15	M 0.20	L 0.24	P 0.80	L 0.10
105	200	D 0.44	C 0.35	B 0.88	0 1.20		0.30	Н 0.18	G 0.27	I 0.48	G 0.30	Н 0.18	F 0.83		N 0.16	M_0.19	г 0.22	P 0.50	L 0.40
104	400	D 0.64		C 0.87	0 0.79	B 0.79	R 0.59	н 0.39	1 0.39		G 0.23	н 0.23	G 0.47	F 0.47	N 0.16	M 0.21	L 0.05	L 0.79	
103	200	D 0.67		c 0.82	B 1.70		R 0.55	н 0.30	I 0.32		н 0.41		G 0.90	-	N 0.10	M 0.28		L 0.75	
102	100	D 0.64		C 0.76	B 1.51		R 0.54	н 0.2	I 0.31		н 0.31		6 0.86		N 0.12	M 0.23		L 0.72	
Sample No.	ISO speed	4th layer		5th layer	6th layer		8th layer	9th layer			10th layer		llth layer		13th layer			14th layer	

[0241]

Subsequently, lens-fitted packaging units were molded using each of the following sample resins.

These were loaded with the samples 101 and 107 to perform test on photographic property.

[0242]

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Figure 1 is an exploded perspective view of a fabricated lens-fitted film unit. Now, the molding of a cartridge and the assembly of a unit will be described. Referring to Figure 1, three members designated as front cover 4, body base 3 and back cover 5 were formed by means of hot-runner-type metal molds. Other parts, which are not described in detail, were assembled into the body, followed by assembly of the front cover. The thus obtained unit was loaded with the above prepared samples 101 and 107. Finally, the back cover was assembled thereinto, thereby obtaining a lens-fitted lightsensitive material packaging unit. This lens-fitted lightsensitive material packaging unit together with a separately supplied explanatory pasteboard was packaged by a packaging machine with the use of a packaging film produced by laminating a polyethylene film with an aluminum foil. The packaging was well-known pillow type packaging whereby a bag configuration was formed with three-way hot melt seal, thereby obtaining a sealed package inhibiting the infiltration of external air.

[0243]

Sample resins 1 to 19 were produced in the following manner, molded into unit members, and assembled into lens-fitted lightsensitive material packaging units, which were packaged with a packaging film. The photographic performance of obtained lens-fitted lightsensitive material packaging units was tested. Each of the resins was molded into the front cover 4, body base 3 and back cover 5.

10 [0244]

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The sample resins were produced according to the following procedures. The extruder employed in the production of sample resins was a vent type single-screw extruder of 100 mm screw diameter and of L/D=28. The extrusion temperature was 230° C.

[0245]

(Preparation of sample resin 1)

A carbon master batch was produced by the known process as described in the Example portion of JP-A-6-130565. Specifically, 49% by weight of carbon black of 1.5 mg/g acetaldehyde gas equilibrium adsorption amount, 8.0 pH and 24 nm average particle diameter, 1% by weight of zinc stearate and 50% by weight of PS natural resin were mixed together and kneaded by means of a Banbury mixer. The mixture was milled by means of mixing rolls, thereby obtaining a rectangular high carbon content resin. Subsequently,

49% by weight of obtained high carbon content resin,
48.5% by weight of PS natural resin, 1.5% by weight of
compound S-26 mentioned above and 1% by weight of zinc
stearate were mixed together, and melted and kneaded by
means of the above vent type single-screw extruder.
Thus, cylindrical carbon master batch M1 was obtained.
The carbon master batch M1 and PS natural resin were
mixed at a ratio of 1:35 and extruded once through an
extruder, thereby obtaining sample resin 1.

10 [0246]

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(Preparation of sample resin 2)

Sample resin 2 was prepared in the same manner as the above sample resin 1, except that, in place of the carbon master batch M1, carbon master batch M2 was produced using a carbon black of 2.1 mg/g acetaldehyde gas equilibrium adsorption amount, 7.5 pH and 16 nm average particle diameter.

[0247]

(Preparation of sample resin 3)

Sample resin 3 was prepared in the same manner as the above sample resin 1, except that the above compound S-1 was employed in place of the compound S-8.

(Preparation of sample resin 4)

Sample resin 4 was prepared in the same manner as the above sample resin 2, except that the above compound S-1 was employed in place of the compound S-8.

[0248]

(Preparation of sample resin 5)

Sample resin 5 was prepared in the same manner as the above sample resin 1, except that the extrusion by means of the same extruder was carried out five times to thereby effect a resin reclamation.

(Preparation of sample resin 6)

Sample resin 6 was prepared in the same manner as the above sample resin 2, except that, as in the preparation of the sample resin 5, the extrusion by means of the extruder was carried out five times to thereby effect a resin reclamation.

[0249]

(Preparation of sample resin 7)

Sample resin 7 was prepared in the same manner as the above sample resin 3, except that, as in the preparation of the sample resin 5, the extrusion by means of the extruder was carried out five times to thereby effect a resin reclamation.

(Preparation of sample resin 8)

Sample resin 8 was prepared in the same manner as the above sample resin 4, except that, as in the preparation of the sample resin 5, the extrusion by means of the extruder was carried out five times to thereby effect a resin reclamation.

25 [0250]

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(Preparation of sample resin 9)
Sample resin 9 was prepared in the same manner as

the above sample resin 1, except that the extrusion by means of the same extruder was carried out four times, followed by 1/30 supplemental addition of the carbon master batch resin M1 and by further extrusion performed once, to thereby effect a resin reclamation.

(Preparation of sample resin 10)

Sample resin 10 was prepared in the same manner as the above sample resin 2, except that the extrusion by means of the same extruder was carried out four times, followed by 1/30 supplemental addition of the carbon master batch resin M1 and by further extrusion performed once, to thereby effect a resin reclamation.

[0251]

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(Preparation of sample resin 11)

Sample resin 11 was prepared in the same manner as the above sample resin 1, except that, in place of the carbon master batch M1, a carbon master batch was produced using a carbon black of 0.6 mg/g acetaldehyde gas equilibrium adsorption amount and 28 nm average particle diameter, thereby obtaining a precursor resin, and except that the extrusion of the precursor resin by means of the same extruder was carried out four times, followed by 1/30 supplemental addition of the carbon master batch resin and by further extrusion performed once, to thereby effect a resin reclamation.

[0252]

(Preparation of sample resin 12)

Sample resin 12 was prepared in the same manner as the above sample resin 1, except that, in place of the carbon master batch M1, a carbon master batch was produced using a carbon black of 3.2 mg/g acetaldehyde gas equilibrium adsorption amount and 12 nm average particle diameter, thereby obtaining a precursor resin, and except that the extrusion of the precursor resin by means of the same extruder was carried out four times, followed by 1/30 supplemental addition of the carbon master batch resin and by further extrusion performed once, to thereby effect a resin reclamation.

[0253]

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(Preparation of sample resin 13)

Sample resin 13 was prepared in the same manner as the above sample resin 1, except that the extrusion by means of the same extruder was carried out four times, followed by supplemental addition of the compound S-26 in the same amount as the reduction thereof caused by pyrolysis during the extrusions and followed by further extrusion performed once, to thereby effect a resin reclamation.

[0254]

(Preparation of sample resin 14)

Sample resin 14 was prepared in the same manner as

the above sample resin 3, except that the extrusion by

means of the same extruder was carried out four times,

followed by supplemental addition of the compound S-1

in the same amount as the reduction thereof caused by pyrolysis during the extrusions and followed by further extrusion performed once, to thereby effect a resin reclamation.

5 [0255]

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(Preparation of sample resin 15)

Sample resin 15 was prepared in the same manner as the above sample resin 1, except that antioxidant S-27 was added and that the extrusion of thus obtained precursor resin by means of the same extruder was carried out four times, followed by supplemental addition of the antioxidant S-27 in the same amount as the reduction thereof caused by pyrolysis during the extrusions and followed by further extrusion performed once, to thereby effect a resin reclamation.

[0256]

(Preparation of sample resin 16)

Sample resin 16 was prepared in the same manner as the above sample resin 1, except that the above compound S-8 was used and that the extrusion of thus obtained precursor resin by means of the same extruder was carried out four times, followed by supplemental addition of the compound S-8 in the same amount as the reduction thereof caused by pyrolysis during the extrusions and followed by further extrusion performed once, to thereby effect a resin reclamation.

[0257]

(Preparation of sample resin 17)

Sample resin 17 was prepared in the same manner as the above sample resin 1, except that the extrusion by means of the same extruder was carried out four times, followed by 1/30 supplemental addition of the carbon master batch resin M1 and further supplemental addition of the compound S-26 in the same amount as the reduction thereof caused by pyrolysis during the extrusions and followed by further extrusion performed once, to thereby effect a resin reclamation.

[0258]

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(Preparation of sample resin 18)

Sample resin 18 was prepared in the same manner as the above sample resin 2, except that the extrusion by means of the same extruder was carried out four times, followed by 1/30 supplemental addition of the carbon master batch resin M2 and further supplemental addition of the compound S-26 in the same amount as the reduction thereof caused by pyrolysis during the extrusions and followed by further extrusion performed once, to thereby effect a resin reclamation.

[0259]

(Preparation of sample resin 19)

Sample resin 19 was prepared in the same manner as the above sample resin 3, except that the extrusion by means of the same extruder was carried out four times, followed by 1/30 supplemental addition of the carbon

master batch resin M1 and further supplemental addition of the compound S-1 in the same amount as the reduction thereof caused by pyrolysis during the extrusions and followed by further extrusion performed once, to thereby effect a resin reclamation.

[0260]

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(Preparation of sample resin 20)

Sample resin 20 was prepared in the same manner as the above sample resin 4, except that the extrusion by means of the same extruder was carried out four times, followed by 1/30 supplemental addition of the carbon master batch resin M2 and further supplemental addition of the compound S-1 in the same amount as the reduction thereof caused by pyrolysis during the extrusions and followed by further extrusion performed once, to thereby effect a resin reclamation.

[0261]

(Preparation of sample resin 21)

Sample resin 21 was prepared in the same manner as the above sample resin 14, except that the extrusion by means of the same extruder was carried out four times, followed by 1/30 supplemental addition of the carbon master batch resin M2 and further supplemental addition of the compound S-1 in the same amount as the reduction thereof caused by pyrolysis during the extrusions and followed by further extrusion performed once, to thereby effect a resin reclamation.

[0262]

The above samples were exposed to light for 1/100 sec using gelatin filter SC-39 manufactured by Fuji Photo Film Co. Ltd., and continuous wedge.

The test on photographic properties were confirmed with those immediately development processed, and those developed after left to stand under the atmosphere at temperature of 45°C and humidity of 60% for 30 days, then open the packaging, and taking the films out of the units.

After the storage of each condition mentioned above, samples were exposed to light for 1/100 sec using gelatin filter SC-39 manufactured by Fuji Photo Film Co. Ltd., and continuous wedge.

15 [0263]

The development was done as follows by using an automatic processor FP-360B manufactured by Fuji Photo Film Co., Ltd. Note that the processor was remodeled so that the overflow solution of the bleaching bath was not carried over to the following bath, but all of it was discharged to a waste fluid tank. The FP-360B processor was loaded with evaporation compensation means described in Journal of Technical Disclosure No. 94-4992.

25 [0264]

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The processing steps and the processing solution compositions are presented below.

(Processing steps)

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5	Step	ŋ	Γime	2	Tempera- ture	Repler rate*	Tank volume						
3	Color development	3 min	5	sec	37.8℃	20 π	nL 1	11.5L					
10	Bleaching		50	sec	38.0℃	5 m	nL	5L					
10	Fixing (1)		50	sec	38.0℃	-		5L					
	Fixing (2)		50	sec	38.0℃	8 m	ıL	5L					
15	Washing		30	sec	38.0℃	17 mI	J 3L						
	Stabili- zation (1)		20	sec	38.0℃	-		3L					
20	Stabili- zation (2)		20	sec	38.0℃	15 mL	ı	3L					
	Drying	1 min	30	sec	60℃								
	*The repleni	shment	ra	te w	as per 1.	lm of a	35-mm w	ride					
	sensitized material (equivalent to one 24 Ex. 1)												
	0]	265]											

The stabilizer and the fixing solution were counterflowed in the order of $(2) \rightarrow (1)$, and all of the overflow of the washing water was introduced to the fixing bath (2). Note that the amounts of the developer carried over to the bleaching step, the bleaching solution carried over to the fixing step, and the fixer carried over to the washing step were 2.5 mL, 2.0 mL and 2.0 mL per 1.1m of a 35-mm wide sensitized material, respectively. Note also that each crossover time was 6 sec, and this time was included in the processing time of each preceding step.

The opening area of the above processor for the

color developer and the bleaching solution were 100 cm 2 and 120 cm 2 , respectively, and the opening areas for other solutions were about 100 cm 2 .

[0266]

The compositions of the processing solutions are presented below.

10	(Color developer) [Tan	k solution] (g)	[Replenisher] (g)
10	Diethylenetriamine pentaacetic acid	3.0	3.0
15	Disodium catecohl-3,5-disulfonate	0.3	0.3
	Sodium sulfite	3.9	5.3
2.0	Potassium carbonate	39.0	39.0
20	Disodium-N,N-bis (2-sulfonatoethyl) hydroxylamine	1.5	2.0
25	Potassium bromide	1.3	0.3
	Potassium iodide	1.3 mg	_
30	4-hydroxy-6-methyl-1,3,3; tetrazaindene	a,7 0.05	-
	Hydroxylamine sulfate	2.4	3.3
35	2-methyl-4-[N-ethyl-N- $(\beta$ -hydroxyethyl)amino] aniline sulfate	4.5	6.5
	Water to make	1.0L	1.0L
40	pH (adjusted by potassium hydroxide and surfuric acid)	10.05	10.18
A E	[0267]		
45	(Bleaching solution) [Tan	k solution] (g)	[Replenisher] (g)
	Ferric ammonium 1,3-	113	170

diaminopropanetetra acetate monohydrate

5	Ammonium bromide	70	105		
3	Ammonium nitrate	14	21		
	Succinic acid	34	51		
10	Maleic acid	28	42		
	Water to make	1.0L	1.0L		
15	pH (adjusted by ammonia water)	4.6	4.0		

[0268]

(Fixer (1) Tank solution)

A 5:95 mixture (v/v) of the above bleaching tank solution and the below fixing tank solution pH 6.8

[0269]

25	(Fixer (2))	[Tank solution]	[Replenisher]
30	Ammonium thiosulfate (750 g/L)	240 mL	720 mL
	Imidazole	7	21
35	Ammonium Methanthiosulfonate	5	15
	Ammonium Methanesulfinate	10	30
40	Ethylenediamine tetraacetic acid	13	39
	Water to make	1L	1L
45	pH (adjusted by ammonia water and acetic acid	7.4	7.45

(Washing water)

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Tap water was supplied to a mixed-bed column filled with an H type strongly acidic cation exchange resin (Amberlite IR-120B: available from Rohm & Haas Co.) and an OH type basic anion exchange resin (Amberlite IR-400) to set the concentrations of calcium and magnesium to be 3 mg/L or less. Subsequently, 20 mg/L of sodium isocyanuric acid dichloride and 150 mg/L of sodium sulfate were added. The pH of the solution ranged from 6.5 to 7.5.

[0271]

15	(Stabilizer)	common to tank replenisher	solution and (g)
	Sodium p-toluenesulfinate		0.03
20	Polyoxyethylene-p-mononon phenylether (average polymerization	•	0.2
25	Sodium 1,2-benzisothiazol	ine-3-on	0.10
23	Disodium ethylenediamine	tetraacetate	0.05
	1,2,4-triazole		1.3
30	1,4-bis(1,2,4-triazole-1-piperazine	ylmethyl)	0.75
	Water to make		1.0 L
35	рН		8.5

[0272]

With respect to the above samples, changes in fog were determined. The measurement results are set forth in Table 3.

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[Table 3]

			ω	0.03	0.03	0.02	0.03	0.09	0.19	0.31	
Table 3		resins	7	0.02	0.03	0.03	0.03	0.10	0.19	0.32	
		Difference in fog of respective sample resins	9	0.03	0.03	0.04	0.04	0.10	0.20	0.32	ned)
		respecti	5	0.04	0.03	0.03	0.04	0.11	0.21	0.33	Table 3 (continued)
	rable 3	n fog of	4	0.02	0.01	0.02	0.03	0.02	0.02	0.02	Table
	ַ	rence i	3	0.03	0.02	0.01	0.02	0.03	0.02	0.03	
		Diffe	2	0.04	0.03	0.02	0.04	0.03	0.02	0.02	
			۲-,	0.03	0.02	0.02	0.03	0.02	0.03	0.04	
0 01		sitive ial	ISO speed	100	200	400	200	640	800	1600	
, 1		Photosensitive material	Sample No.	102	103	104	105	106	107	101	
							4	_			_

	— т	$\neg \tau$				7-5	—Т	
	21	0.02	0.02	0.01	0.02	0.02	0.02	0.02
	11 12 13 14 15 16 17 18 19 20	0.02	0.02	0.02 0.02 0.03 0.02 0.02 0.02 0.02 0.03 0.03	0.02 0.02 0.02 0.03 0.02 0.02 0.02 0.02		0.02	0.02
	19	0.02	0.02	0.03	0.02	0.02	0.03	0.03
resins	18	0.03	0.02	0.03	0.02	0.03	0.03	0.04
sample	17	0.02	0.03	0.02	0.02	0.03	0.04	0.05
ctive	16	0.03	0.03	0.02	0.02	0.05	0.08	0.09
Difference in fog of respective sample resins	15	0.03 0.02 0.03 0.02 0.03 0.03 0.03 0.03	0.02 0.02 0.02 0.03 0.03 0.03 0.02 0.02	0.02	0.02	90.0	0.11 0.08 0.11 0.07 0.12 0.08 0.04 0.03 0.03 0.02	0.13
fog o	14	0.02	0.02	0.02	0.03	0.05	0.07	0.08
ence in	13	0.03	0.02	0.03	0.02	0.06	0.11	0.14
Differ	12	0.02	0.02	0.02	0.02	0.04	0.08	0.15 0.09 0.14 0.08 0.13 0.09 0.05 0.04 0.03 0.02
	11	0.03	0.02	0.02	0.02	0.06	0.11	0.15
	10	0.02	0.03	0.02	0.03	0.05	0.09	0.10
	6	0.03	0.03 0.03	400 0.03 0.02	0.03	640 0.06 0.05	0.12	0.14
nsitive	ISO	100	200	400	500	640	800	1600 0.14
Photosensitive material	Sample No.	102	103	104	105	106	107	101

: Present invention

[0274]

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It is apparent from the Table that, samples having ISO speeds of 640 or more show very large changes in fog by the use of reclaimed resins. Contrarily, samples having ISO speeds of 640 or less show small influence of the variation in fog. It is apparent that reduction in fog variation was observed by the supplemental addition of carbon black or a compound to suppress the generation to the reclaimed resins. It is apparent that although single addition of carbon black or the compound can attain the advantages, supplemental addition of the both is more preferable.

[0275]

It is apparent that the acetaldehyde gas equilibrium adsorption amount of carbon black is preferably 2 mg/g or more, and the molecular weight of the compound is preferably 230 or more.

[0276]

(Example 2)

Samples 201 to 213 as specified in Table 4 were produced in the same manner as the sample 104 of Example 1, except that the silver content was changed by changing the amount of emulsion in the 4th, 5th, 6th, 8th, 9th, 10th, 11th, 13th and 14th layers.

25 [0277]

In the production thereof, the silver content and gelatin quantity in each of the layers were altered so

as to attain desired ISO speed and film thickness.

The samples 201 to 213 were charged into lens-fitted packaging units wherein the same sample resins as in Example 1 were employed to thereby obtain lens-fitted lightsensitive material packaging units, and the same photographic performance evaluation was conducted, thereby determining fog variations. The measuring results are listed in Table 4.

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	8	0.03	0.03	0.02	0.09	0.14	0.18	0.23	0.30	0.41	0.19	0.19	0.21	0.50
resins	7	0.02	0.03	0.03	0.10	0.15	0.18	0.23	0.30	0.41	0.19	0.19	0.20	0.49
ve sample	9	0.03	0.03	0.02	0.10	0.16	0.19	0.24	0.30	0.42	0.20	0.20	0.20	0.51
respective	5	0.02	0.03	0.03	0.11	0.16	0.19	0.24	0.31	0.43	0.21	0.21	0.22	0.51
fog of	4	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.02	0.02	0.02	0.02	0.04
Difference in	3	0.03	0.02	0.03	0.03	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.02	0.04
Diffe	5	0.02	0.03	0.02	0.03	0.02	0.02	0.03	0.03	0.03	0.02	0.02	0.02	0.04
	T.	0.03	0.02	0.02	0.02	0.03	0.03	0.03	0.04	0.03	0.03	0.03	0.03	0.05
erial	Film thickness \$\mu\$m	21.8	21.8	21.9	21.9	21.9	21.9	21.9	21.9	21.9	21.9	23.4	23.8	21.9
ive mat	ISO	400	400	500	500	200	500	500	500	200	640	640	800	500
Photosensitive materi	Silver amount g/m ²	4.52	5.01	5.95	6.03	6.90	7.72	8.12	9.03	9.95	6.90	6.90	7.72	10.21
Phc	Sample No.	201	202	203	204	205	206	207	208	209	210	211	212	213

nued)	
(continue	
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Table	

Table 4 (continued) Difference in fog of respective sample resins	21	0.02	0.02	0.02	0.02	0.05	0.02	0.03	0.06	0.12	0.02	0.02	0.02	0.49
	20	0.03	0.02	0.02	0.02	0.02	0.02	0.03	0.06	0.12	0.02	0.02	0.02	0.48
	19	0.02	0.03	0.03	0.02	0.02	0.03	0.04	0.08	0.15	0.03	0.03	0.03	0.48
	18	0.03	0.02	0.03	0.03	0.03	0.03	0.04	0.08	0.17	0.03	0.03	0.03	0.48
	17	0.02	0.03	0.02	0.03	0.03	0.04	0.05	0.10	0.21	0.04	0.04	0.04	0.49
	16	0.03	0.03	0.02	0.05	90.0	0.07	0.09	0.16	0.27	0.07	0.08	0.08	0.48
	15	0.02	0.03	0.02	90.0	0.09	0.11	0.14	0.20	0.32	0.11	0.11	0.12	0.50
	14	0.02	0.02	0.02	0.05	90.0	0.07	0.10	0.15	0.27	0.07	0.07	0.07	0.48
	13	0 03	-	0.03	0.06	0.08	0.10	0.14	0.20	0.33	0.12	0.12	0.11	0.49
	12	000	0.02	0.02	0.04	0.06	80.0	0.10	0.17	0.29	0.09	0.09	0.08	0.49
	111	0.03	0.02	0.02	90.0	0.08	0.10	0.15	0.20	0.35	0.10	0.10	0.11	0.50
	10	000	0.03	0.02	0.05	0.07	0.08	0.12	0.18	0.30	0.10	0.09	0.09	0.49
	6	0.0	0.03	0.03	90.0	0.09	0.11	0.15	0.21	0.34	0.12	0.12	0.12	0.49
Photosensitive material	Film thickness	μμ	• 1 •		21.9	21.9	21.9	21.9	21.9	1 .	21.9	23.4	23.8	21.9
	ISO	5 00 8	400	200	200	500	500	500	500	500	640	640	800	200
	Silver	g/m ²	4.32	5.95	6.03	6.90	7.72	8.12	9.03	9.95	6.90	6.90	7.72	10 01
OHO	Sample		202	203	204	205	206	207	208	209	210	211	212	21.2

: Present invention

[0279]

It is apparent from the Table that, when reclaimed resins are employed, the fog variation is extremely large with respect to the samples of 6 g/m^2 or more silver content, but the effect of fog variation is slight with respect to the samples of less silver content.

It is also apparent that, with respect to the samples of 6 to $10~\rm g/m^2$ silver content, the fog variation is reduced by the same supplemental addition of carbon black and a compound capable of suppressing the generation of harmful gases as in Example 1.

[0280]

(Example 3)

Samples 301 to 314 having different film thicknesses as specified in Table 5 were produced in the same manner as the sample 203 of Example 2, except that the amount of gelatin was altered in each of the layers.

20 [0281]

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The silver content of each of the layers was altered so as to attain desired ISO speed and silver quantity.

The samples 301 to 314 were charged into lensfitted packaging units wherein the same sample resins as in Example 1 were employed to thereby obtain lensfitted lightsensitive material packaging units, and the same photographic performance evaluation as in Example 1 was conducted, thereby determining fog variations and further determining fog unevenness.

[0282]

5 The fog unevenness was determined by visually inspecting the samples after processing. The measuring results are listed in Table 5.

[0283]

[Table 5]

Table 5

									_	_			~	-		_	
Г		21	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
S		20	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
		19	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
sin		18	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
re		17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
ole		16	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
samp		15	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
ve Ve		14	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
cti		13	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
spe		12	0	0	0	0	0	0	0	0	0	0	0	0	0	0	e d
re		11	0	0	0	0	0	0	0	0	0	0	0	0	0	0	erat
o f		10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	generated generated
SSS		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	g g g g
nne		æ	0	0	0	0	×	×	×	×	×	×	×	×	X	×	fog fog rate
uneve		7	0	0	0	0	×	×	×	×	×	×	×	×	×	×	uneven fog uneven fog g generated
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			0	0	0	0	0	0	0	0	0	0	0	0	0	0	I O
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+] E	nes		0	0	ω.	-	7	8.	ω	25.5	8	28.3	ω.	24.1	24.8	nen nen
100	Film	thickness	18.0	19.9	20.9	21.8	22.1	23.2	23	24.8	25	26.8	28	23	24	24	orer orer
100		th	\perp		_			 	_	-	-	-	-	-	-	-	<pre>③: Increment O: Increment x: Increment</pre>
Dhotosopeitivo		ple 	=	2	303	304	305	306	307	308	309	310	311	312	313	314	@O×
		Sample No.	301	302	3 8	3	7	il m) ñ) m	۱ ñ	m	m	m	m	٣	
L			Щ.	_L			Т.		_1		1						_

Present invention

[0284]

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As apparent from Table 5, a slight fog increase by the use of reclaimed resin is recognized with respect to all the samples. Although a uniform fog increase is recognized with respect to samples of 22 μ m or less film thickness, an uneven fog unfavorably occurs with respect to samples of more than 22 μ m film thickness. It has been found that the supplemental addition of carbon black and a compound capable of suppressing the generation of harmful gases renders the fog increase uniform with respect to samples of more than 22 μ m film thickness as well.

[02851

(Example 4)

In the samples prepared in Examples 1, 2, and 3 the support of Example 3 of JP-A-10-293373 was employed in place of the support of cellulose triacetate film, and the samples were formed into APS Format cartridges. The sample resins 1 to 21 were used in the body of Utsurundesu (Quick Snap) Super Eye 800 Flash 25 produced by Fuji Photo Film Co., Ltd., and evaluations were effected. Similar results were obtained with respect to all of the Examples 1, 2, and 3.

[Brief explanation of Drawing]

25 [Figure 1]

Figure 1 is an exploded perspective view of lensfitted film unit which constitutes one form of the lightsensitive material package of the present invention.

[Explanation of symbols]

- 2: Film unit body; 3: Body base; 4: Front cover; 5:
- Rear cover; 6: Exposure unit; 10: Patrone chamber; 11:
 - Film role chamber; 12: patrone; 13: Photographic film.

[Name of Document] Abstract
[Abstract]

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[Object] To provide a lightsensitive material package wherein a molding containing a substance capable of 5 adsorbing harmful substances, in particular gasified harmful substances, in reclaimed resins or capable of suppressing the occurrence thereof, which molding has thus no adverse effects on a photographic lightsensitive material, in particular a high-speed lightsensitive material and a photographic 10 lightsensitive material containing a large silver amount used and a photographic lightsensitive material having a large thickness, is accommodated in order to expand the use of reclaimed resins in plastic material 15 members.

[Means to solve] A lightsensitive material package comprising a silver halide color photographic lightsensitive material having at least one each of a red-sensitive, green-sensitive and blue-sensitive silver halide emulsion layer on a support and having ISO speed of 640 or more, the silver halide color photographic lightsensitive material being arranged in a common gas-phase atmosphere and sealed in the lightsensitive material package together with a plastic material member, characterized in that the plastic material member is that produced from a resin to which a substance capable of adsorbing a substance having an

adverse effect on a photographic property has been supplementally added prior to molding thereof.

[Elected drawing] None

[Name of Document) Drawing
[Figure 1]

